

AD620940

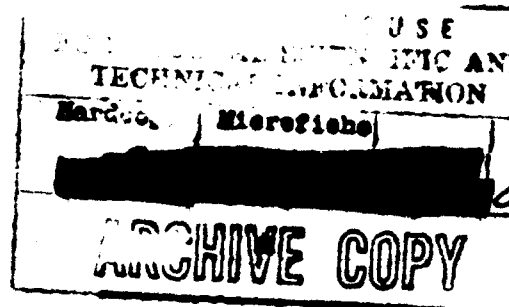
RADC-TR-64-569
Final Report



DETECTION OF LIQUID CRYSTAL GASES
(REACTIVE MATERIALS)

J. L. Fergason
N. N. Goldberg
C. H. Jones
et al
(Westinghouse)

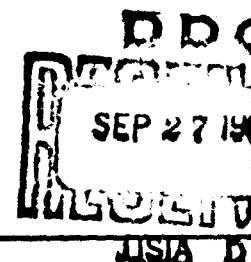
TECHNICAL REPORT NO. RADC-TR-64-569
August 1965



QRC Branch
Rome Air Development Center
Research and Technology Division
Air Force Systems Command
Griffiss Air Force Base, New York

Best Available Copy

20050301019



FOREWORD

This report was prepared by Westinghouse Electric Corporation, Pittsburgh, Pa. under Air Force Contract AF30(602)-3306 (Project 5534, Task 553402), "Detection of Trace Quantities of Contaminant Gases in the Atmosphere." The authors acknowledge the guidance and assistance of Lt. V. Rice, the Rome Air Development Center Contract Monitor.

The work reported began 1 February 1964 and was concluded 12 November 1964. It was directed by J. L. Ferguson for the Westinghouse Electric Corporation. Other contributors to the report were N. N. Goldberg, C. H. Jones, R. S. Runk, L. C. Scala, and F. Davis. The work was performed at the Research Laboratories in the Applied Physics Department, R. E. LaCroix, Manager.

Additional information on this subject can be obtained by contacting Lt. Vincent N. Rice, Rome Air Development Center, (EMICA), Griffiss AFB, New York.

This technical report has been reviewed and is approved.

Approved:

Vincent N. Rice
for ROBERT D. BYRNE
Project Engineer

Approved:

Robert J. Quinn, Jr.
ROBERT J. QUINN, JR.
Colonel, USAF
Chief, Intelligence & Information Processing Division

FOR THE COMMANDER:

Irving J. Gabelman
IRVING J. GABELMAN
Chief, Advanced Studies Group

ABSTRACT

A set of reactive liquid crystal materials were developed which are capable of detecting quantities (10 ppm or less) of HCl, HF, hydrazine, UDMH, and nitrogen dioxide. The materials exhibit a change in color transition temperature upon exposure to these contaminants gases or vapors. Except for HF and HCl, the contaminants are readily distinguished from each other.

CONTENTS

1. SUMMARY	1
2. INTRODUCTION.	5
3. DETECTION OF TRACE HCl AND HF	7
3.1 Introduction and Theory.	7
3.2 Screening Tests.	12
3.3 Sensitivity Tests.	13
3.4 Conclusions.	26
3.5 References	30
4. DETECTION OF TRACE NITROGEN OXIDES.	31
4.1 Introduction and Theory.	31
4.2 Screening Tests.	34
4.2.1 Methods and Apparatus	35
4.2.2 Materials	36
4.2.3 Results	39
4.3 Sensitivity Tests.	41
4.4 Conclusions.	47
4.5 References	52
5. DETECTION OF TRACE HYDRAZINE AND UDMH	53
5.1 Introduction and Theory.	53
5.2 Screening Tests.	61
5.3 Sensitivity Tests.	63
5.4 Conclusions.	70
5.5 Reference.	71

6. DETECTION OF TRACE HNO_3	73
7. CONCLUSIONS AND RECOMMENDATIONS	75

Appendix I: BACKGROUND INFORMATION ON LIQUID CRYSTALS.	77
I.1 Introduction	77
I.2 Optical Effects.	77
I.3 Molecular Structure.	80
I.4 Temperature Measurements	83
I.5 Temperature Sensitivity in Gas Detection	91
I.6 Effect of Thickness.	94
I.7 References	95

Appendix II: CHEMICAL PREPARATION OF MATERIALS.	97
---	----

Appendix III: VOLUMETRIC DILUTION APPARATUS.	111
--	-----

Appendix IV: APPLICATION OF LIQUID CRYSTAL DETECTORS.	115
---	-----

FIGURES

3.1 Vapor pressure of 4.84% aqueous solution of HCl (1.614 N).	18
3.2 Vapor pressure of 5.28% aqueous solution of HCl (1.760 N).	19
3.3 Vapor pressure of 10.3% aqueous solution of HCl (3.433 N).	20
3.4 Apparatus for exposure of a liquid crystal film to HCl and HF vapors.	21
3.5 Effect of 15 min exposure by HCl on Matrix A + 4% Oleyl Amine.	25
3.6 Effect of 15 min exposure by HF on Matrix A + 4% Oleyl Amine.	28

4.1	Screening test to determine the best matrix for NO ₂ detection	37
4.2	Effects of exposing selected NO ₂ detectors to HCl, UDMH, and HF.	38
4.3	Effect of 15 minutes exposure of Matrix A to 1000 ppm of NO ₂	44
4.4	Effect of 15 minutes exposure of Matrix A to 6 ppm of nitrogen dioxide + methyl linoleate and effect of 24 hrs. aging on exposed sample	45
4.5	Effect of exposure of 6 ppm of nitrogen dioxide on Matrix A + methyl linoleate for different exposure times	46
4.6	Effect of 15 minutes exposure of 1000 ppm of nitrogen dioxide on Matrix A plus different concentrations of oleic acid . . .	48
4.7	Effect of 15 minutes exposure of 100 ppm of nitrogen oxide on Matrix A plus different concentrations of oleic acid.	49
4.8	Effect of 15 minutes contamination by 10 ppm of nitrogen dioxide on Matrix A added with different concentrations of oleic acid.	50
4.9	Effect of 15 minutes exposure of 6 ppm of nitrogen dioxide on Matrix A plus different concentrations of oleic acid.	50
4.10	Effect of exposure time of Matrix A with 3% concentration of oleic acid exposed to 6 ppm of nitrogen dioxide	51
5.1	Effect of 15 min contamination by 8 ppm UDMH on Matrix A + 4% Cholesteryl Isophthalyl Chloride	66
5.2	Effect of 15 min exposure by 8 ppm UDMH on Matrix A + 4% Cholesteryl Terephthalyl Chloride	67
I.1	Schematic representation of helical model of the cholesteric phase	79
I.2	The structural formula of cholesterol	81
I.3	Apparatus for measuring the temperature sensitivity of cholesteric liquid crystals	84
I.4	Temperature as a function of wavelength for cholesteryl nonanoate and cholesteryl decanoate.	85

I.5	Temperature as a function of wavelength for a number of cholesteric materials added to cholesteryl nonanoate	86
I.6	Temperature vs wavelength of four closely related materials added to cholesteryl nonanoate	88
I.7	Temperature sensitivity of Figure A.6 materials.	89
I.8	Temperature vs wavelength for liquid crystal material containing several oil soluble additives	90
I.9	Temperature characteristics of cholesteryl chloride and cholesteryl nonanoate mixtures in various proportions.	92
III.1	Volumetric dilution apparatus.	111

TABLES

1.1	Summary of Best Detection Materials.	2
1.2	Observation of Detection Materials at a Single Temperature.	3
3.1	Basic Strength of Aliphatic Amines and Ammonia	8
3.2	Materials Prepared for the Detection of HCl and HF	14
3.3	Additives Tested for the Detection of HCl and HF	15
3.4	Temperature Shift (°C) of 4% Oleyl Amine in 60/40 Cholesteryl Nonanoate/Cholesteryl Oleyl Carbonate Exposed to HCl	24
3.5	Temperature Shift (°C) of 4% Oleyl Amine in 60/40 Cholesteryl Nonanoate/Cholesteryl Oleyl Carbonate Exposed 15 Min to HF in Water.	24
3.6	Detection of HCl with 4% Normalized Oleyl Nicotinate in 60/40 Cholesteryl Nonanoate/Cholesteryl Oleyl Carbonate.	27
3.7	Detection of HF with 4% Normalized Oleyl Nicotinate in 60/40 Cholesteryl Nonanoate/Cholesterol Oleyl Carbonate.	27
3.8	Detection of HCl with 4% Oleyl Isonicotinate in 60/40 Cholesteryl Nonanoate/Cholesteryl Oleyl Carbonate.	29
3.9	Detection of HF with 4% Oleyl Isonicotinate in 60/40 Cholesteryl Nonanoate/Cholesteryl Oleyl Carbonate.	29

4.1	Reactivity of Five Liquid Crystal Matrices to Four Gases.	41
5.1	Materials Screened for UDMH, Hydrazine Detection	62
5.2	Detection of UDMH with 4% Cholesteryl Terephthalyl Chloride in 60/40 Cholesteryl Nonanoate-Cholesteryl Oleyl Carbonate .	65
5.3	Detection of UDMH with 4% Cholesteryl Isophthalyl Chloride in 60/40 Cholesteryl Nonanoate-Cholesteryl Oleyl Carbonate .	65
5.4	Detection of UDMH with 4% Cholesteryl Chloroformate + Cholesterol in 60/40 Cholesteryl Nonanoate-Cholesteryl Oleyl Carbonate for Thick and Thin Films	68
5.5	Detection of UDMH with 4% Cholesteryl Chloroformate + Oleyl Alcohol in 60/40 Cholesteryl Nonanoate-Cholesteryl Oleyl Carbonate.	68
I.1	Varying Chain Lengths and Cholesteric Phases of Cholesteryl Esters	82
I.2	Response of Liquid Crystals to Various Solvent Vapors. . . .	93
IV.1	List of Reactive Materials Supplied.	118

1. SUMMARY

The purpose of this contract was to determine whether reactive liquid crystals could be developed that would detect 1 to 10 ppm of certain gases.

Satisfactory materials were produced to detect hydrazine hydrate (HH), unsymmetrical dimethylhydrazine (UDMH), NO_2 , HNO_3 , HF, and HCl. With the exception of HCl and HF, all of the gases could be readily distinguished from one another.

Temperature-sensitive detectors were developed which are capable of distinguishing between HH and UDMH at concentrations of 8 ppm.

A number of detectors were developed that respond to the oxides of nitrogen, and detection of 6 ppm of NO_2 was satisfactorily achieved. N_2O , which is relatively inert, was found not to react with any of the systems studied.

When oxides of nitrogen are present in an atmosphere that contains any water vapor, HNO_3 will be formed. Hence it was deemed wise to obtain a detector of HNO_3 , although this was not specifically called for in the contract. Materials that detected 1 ppm were prepared and tested.

Two detectors were developed that will detect HCl and HF at concentrations below 1 ppm. However, no simple method for distinguishing between the two was found.

Tables 1.1 and 1.2 summarize the results obtained with the best detection materials developed. The rectangles in the tables

indicate the nature and degree of the effect when a detecting material produces a strong reaction to one of the gases. Because of lack of time, certain materials were not tested with all of the gases. These are indicated by "NT" in the tables.

For gas detection a 1-mil cholesteric liquid crystal film is prepared on one side of a thin Mylar film, and the other side of the film is sprayed with a black paint. At room temperature this film will reflect little light and hence will appear black. If the film is slowly heated it will reach a temperature at which it reflects red light, so it appears red if viewed by sunlight or incandescent light. This temperature is called the "red temperature." A further increase in temperature causes it to turn orange, then yellow, then green, then blue, and finally black again. The process is reversible, so as the film is cooled the predominant wave length of the reflected light varies from the short wavelength blue to the long wavelength red. Now if some gas reacts with the liquid crystal matrix the red color may occur at a different temperature. This is illustrated for a variety of gases and a variety of liquid crystal detectors in Table 1.1. For

Table 1.1 - Summary of Best Detection Materials.

Symbol	A	E	L	M	N	O	J
Liquid Crystal Detection Material	60% Cholesteryl Nonanoate 40% Cholesteryl Oleyl Carbonate	97% A 3% Oleic Acid	96% A 4% Oleyl Amine	96% A 4% Monocholesteryl Terephthalyl Chloride	96% A 4% Cholesteryl Phenyl Hydrazide	80% A 7% Cholesterol 7% Cholesteryl Chloroformate	96% A 4% Methyl Linolenate
Red Temperature of Uncontaminated Material	39.2°	32°	29 °C	44°	39°	Green (not Temp. sensitive)	25.9°
Change in red temperature due to 15 min. exposure to trace contaminants at 20 °C	HCl (8 ppm)	0	+12 °C	0	0	No Color Change	NT
	HF (8 ppm)	0	+12 °C	0	0	No Color Change	NT
	Hydrazine (8 ppm)	0	0	All first a negative shift that later goes positive	0	Red A Permanent Color Shift	NT
	UDMH (8 ppm)	0	0	-2°	0	Red A Permanent Color Shift	NT
	NO ₂ (6 ppm)	-0.1°	-0.3°	NT	0	No Color Change	-3.3°
	HNO ₃ (8 ppm)	0	0	NT	0°C	>+1 °C	NT

* NT, not tested

example, when material M is reacted with 8 ppm of UDMH for 15 min, the red temperature is reduced by 2°C.

Table 1.2 illustrates a detection method for circumstances in which no accurate means of temperature measurement is practical. For example, to test for UDMH one takes two sample patches of material

Table 1.2 - Observation of Detection Materials at a Single Temperature.

Symbol	A	E	L	M	N	O**	J
Liquid Crystal Detection Material	60% Cholesteryl Nonanoate 40% Cholesteryl Oleyl Carbonate	97% A 3% Oleic Acid	96% A 4% Oleyl Amine	96% A 4% Monocholesteryl Terephthalyl Chloride	96% A 4% Cholesteryl Phenyl Hydrazide	86% A 7% Cholesterol 7% Cholesteryl Chloroformate	96% A 4% Methyl Undecanoate
Sample Temperature	40°C	33°C	30°C	45°C	36°C	20° to 30°C	29°C
Color of Uncontaminated Sample of Material	Green	Green	Green	Green	Green	Green	Green
New color due to 15 min. exposure to trace contaminants at 20°C	HCl	No Change	Red 0.5 ppm	No Change	No Change	No Change	NT
	HF	No Change	Red 0.5 ppm	No Change	No Change	No Change	NT
	Hydrazine	No Change	No Change	Red* 8 ppm	No Change	Red 8 ppm	NT
	UDMH	No Change	No Change	Blue 4 ppm	No Change	Red 8 ppm	NT
	NO ₂	Blue Green 120 ppm	Blue Green 10 ppm	NT*	No Change	No Change	Blue 3 ppm
	HNO ₃	No Change	No Change	NT	Red 1 ppm	No Change	NT

* Immediately after response the color shift is toward the blue. The color shift then reverses and after a day it becomes red.

* NT, not tested

** Not temperature sensitive

M. One patch is exposed to 4 ppm of UDMH for 15 min and the other is kept unexposed as a control. Then the two are heated together until the control turns green, at which time the exposed patch will shift to blue.

About This Report. Sections of this report discuss in detail the problems of developing detectors for each of the gases. The screening tests and the sensitivity tests used for each gas are described.

General background on liquid crystals and their use as detectors is given in Appendix I. Their molecular structure and usual optical properties are discussed at some length.

Details of the chemical preparation of 28 materials that are used in the preparation of various liquid crystal detectors are given in Appendix II.

A description of the apparatus that was used for volumetric dilution will be found in Appendix III.

Appendix IV explains how samples of solutions of liquid crystal detecting materials can be prepared for exposure to an atmosphere containing contaminant gas, and how the films may be tested. Table IV.1 lists all of the materials that were delivered to RADC.

2. INTRODUCTION

Liquid crystal materials may be used for the detection of small quantities of reactive chemical vapors. The following factors are fundamental to this application:

a) A liquid crystal system can be prepared which has a given color over a broad range of temperatures, and the temperature sensitivity may be varied as desired. As an example of this, consider the cholesteric system composed of cholesteryl oleyl carbonate (OCC) and cholesteryl nonanoate (CN) which shows a variation in the temperature of operation from 20.5°C for pure OCC through all temperatures (for varying mixtures of these two materials) up to 70°C for pure CN.

b) Materials soluble in the liquid crystal phase when mixed in small amounts with the liquid crystal system will change the color vs. temperature relationship of the system by a predictable amount. The solubility pre-requisite of the additive is not too great a limiting factor, since almost all oil soluble compounds will be soluble in the liquid crystal matrix.

c) The color of the liquid crystal system is a function of the shape and polarity of the molecules of which it is composed. This effect appears to occur as an averaging effect so that the wavelength of maximum scattering of the color of a liquid crystal system will be affected by all the constituents. Thus, if an oil soluble material, whose shape or polar properties may be changed by a specific chemical reaction, is added to a liquid crystal matrix: 1) the system will be sensitive (reactive) to a specific vapor (or vapors); 2) the sensitivity will manifest itself as a change in the color of the liquid crystal system; and 3) the effects will be permanent or nonpermanent depending upon the chemical reaction or reactions involved. This phenomenon occurs even though the original oil soluble additive does not change color when it alone chemically reacts with the vapor.

It is in this fashion that the liquid crystal matrix serves as a sensitive indicator. For useful applications it is necessary to find liquid crystal systems with materials dissolved in them which will react with specific vapors so as to produce easily identifiable colors at or near room temperature.

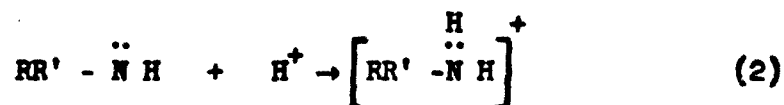
The work associated with developing specific detectors for each of the gases is found in the following sections.

3. DETECTION OF TRACE HCl AND HF

3.1 INTRODUCTION AND THEORY

In the detection of acidic vapors, e.g., hydrochloric acid and/or hydrofluoric acid vapors, an acid-base type of reaction seemed of prime interest. The general theory of acids and bases as proposed by G.N. Lewis was to define bases as substances having unshared electron pairs that can be donated to form coordinate (shared) covalent bonds. He defines an acid as a substance having at least one atom that can accept or receive into its valence shell an electron pair belonging to another atom with bond formation as the result.

In this investigation the base portion of the acid-base type reaction has been organic amino compounds, and more specifically, the nitrogen atom with its unshared electron pair present in these amines. The amino compounds can be used as additives to the liquid crystal matrix, or they may be synthesized as integral parts of the liquid crystal system itself. The acid portion of the reactions to be considered is the proton from the halogen acids which can avail itself of the unshared pair of electrons on the amino nitrogen atom for bond formation. In these cases the reaction products are substituted ammonium-type derivatives. For example



Depending upon whether the amine is primary (1), secondary (2), or tertiary (3), the products of reaction are those shown above.

Varying the degree of substitution as well as the types of substituent groups of the nitrogen atom in the amine is known to affect the base strength of the molecule. Consider the protonation by water of some aliphatic amines and ammonia (Table 3.1). Here we see that the relative strengths of these basic materials vs. hydrogen acids in aqueous systems are in the order shown. In general then, it can be said that the result of replacing the hydrogen atoms of ammonia with alkyl (R) groups is to increase the basic strength. The effect of alkyl groups is clearly to make the unshared pair of electrons on nitrogen more available to an electrophilic substance (e.g., the proton) that is, the alkyl groups increase the electron density on the nitrogen atom. This effect of the alkyl groups is referred to as an inductive effect and is a reflection of the unequal sharing of the electrons in the C-N bond, with the result that nitrogen is relatively more electron rich in RNH_2 than in NH_3 .

Table 3.1 - Base Strength of Aliphatic Amines and Ammonia

<u>Name</u>	<u>Structure</u>	<u>Base Strength</u>
Ammonia	NH_3	4.75
Trimethyl Amine	$(\text{CH}_3)_3\text{N}$	4.20
Methyl Amine	CH_3NH_2	3.37
Triethyl Amine	$(\text{CH}_3\text{CH}_2)_3\text{N}$	3.36
Ethyl Amine	$\text{CH}_3\text{CH}_2\text{NH}_2$	3.27
Dimethyl Amine	$(\text{CH}_3)_2\text{NH}$	3.22
Diethyl Amine	$(\text{CH}_3\text{CH}_2)_2\text{NH}$	2.89

Further consideration of the data in Table 3.1 illustrates other important structural effects. Thus, although the replacement of the hydrogen atoms of ammonia by alkyl groups causes an increase in base strength, triethylamine is weaker, rather than stronger, than diethylamine. This is readily explained by considering the tetrahedral

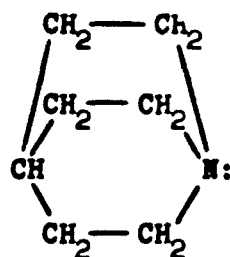
configuration that the protonated ammonia (NH_4^+) or amine $[(\text{CH}_3\text{CH}_2)_3\text{NH}^+]$ assumes. The presence of three bulky CH_3CH_2 groups causes some crowding of these groups when they are forced into the tetrahedral configuration. This mutual interaction involves repulsive forces that oppose the attachment of the proton. Thus, the tendency to accept the proton is reduced, and the base strength is less than it would be expected to be.

Another structural effect need be considered. Trimethylamine, $(\text{CH}_3)_3\text{N}$, is a somewhat weaker base (see Table 3.1) than triethylamine, $(\text{C}_2\text{H}_5)_3\text{N}$, with respect to protonation (that is, base strength values are equilibrium constants for protonation by water). However, it is noteworthy that the Lewis-type acid trimethylboron, $\text{B}(\text{CH}_3)_3$, forms a more stable complex with trimethylamine than triethylamine. This result can be accounted for by examining molecular models of these addition-type



compounds. In the triethylamine complex (5) the interference between the ethyl groups and the methyl groups on the boron atom promotes dissociation of the complex. In the trimethylamine complex (4) this interference is somewhat less, and so the complex is more stable. Thus, the trimethylamine is a stronger base towards trimethylboron than is triethylamine.

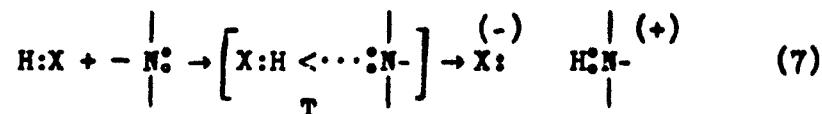
Both of the foregoing structural effects are often referred to as steric factors and are concerned with the spatial requirements of the molecules involved in specific reactions and series of reactions. To more clearly illustrate the necessity of close consideration of spatial requirements consider the role played by steric interference of the type just discussed on the tertiary amine quinuclidine (6).



(6)

Quinuclidine, which structurally approximates triethylamine, forms a compound with trimethylboron that is more stable than $(\text{CH}_3)_3\text{N}^+ - \text{B}^-(\text{CH}_3)_3$. The folding back of the carbon chains attached to nitrogen as a result of their presence in the cage-like ring system reduces interference with the methyl groups and contributes to stability in the complex. Thus, depending on the reactions and the reactants involved, different orders of increasing or decreasing basicity (or acidity) can be obtained.

In the vapor phase detection of acidic vapors like hydrochloric (HCl) and hydrofluoric (HF) acids, the protonation reaction of a base will differ from that of an aqueous system, in that acid and/or base strengths may vary. In aqueous systems, the only acid that need be considered is the protonated water molecule (H_3O^+), and its strength is constant. Considerations of the acid strengths of the two acids to be detected and differentiated from each other should indicate the base strengths of the amines to be used. Under the conditions employed for the detection of HCl and HF, the former is the stronger acid. This is due primarily to the manner in which dissociation occurs and can be depicted as follows. In the vapor state, the associated HX molecule approaches the electron pair on the nitrogen atom of the amine to form a transition type complex (T):



As dissociation occurs, the hydrogen atom is captured by the nucleophilic nitrogen atom to form an ammonium type complex. Thus, since the dissociation energy of HCl is lower (102 K cal/mole) than

that of HF (135 K cal/mole), then HCl manifests itself as the stronger acid. Gaseous HF exists to a large degree in the associated state; i.e., molecules of HF are associated. This can be readily explained by the greater tendency for hydrogen bonding which HF exhibits as compared to HCl.

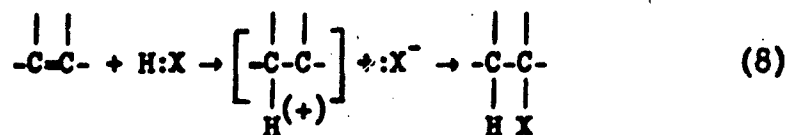
Thus, as stated earlier, not only must the reactions involved be carefully examined but also the reactants before any order of reactivity or selectivity can be established. If an acid-base scale is to be determined, careful considerations must be given to: (a) the molecular structure of the various species involved so as to preclude discrepancies arising from spatial requirements (steric factor) and (b) the anticipated reactions so that similar and identical reactions are compared (as opposed to, e.g., protonation in aqueous and non-aqueous systems).

Since protonation in the vapor phase was the reaction under consideration, then it appeared that all that was required for identification and/or differentiation of HCl and HF was an amine of the appropriate basicity and spatial requirements. As concerned the steric factor, it could be eliminated since in both instances the same moiety was involved, namely, the proton. Therefore, any effect due to this factor would be similarly evident in both cases. To determine the appropriate basicity for both detection and identification a screening technique was employed using commercially available materials in addition to those prepared in these laboratories. It was anticipated that there would be found nitrogen-containing amines which were of such structures and composed of such groups that would allow for the simple and direct detection and identification of both HCl and HF.

In addition to, and possibly in conjunction with, this acid-base type of detection, the literature was screened for both qualitative and quantitative analytical reagents that might serve as detectors. The one major problem was the prerequisite of oil solubility. None of the inorganic analytical reagents could be readily dissolved in the liquid crystal matrix. An examination of the literature on organic analytical reagents did not produce many oil soluble reagents; actually,

only one reagent appeared to be useful, triphenyl tin chloride¹.

Another possible means of differentiating between HCl and HF that was considered was the difference in the rates of addition of the hydrogen halides to unsaturated compounds, e.g., olefins (>C=C<). Since these reactions would occur



with the acids in their vapor state then a difference in reactivity would be noted which would be due to the ionization difference of the two hydrogen halides. To be sure, the nucleophilic character of the olefin will play a part in this ionization, but it will be a constant for both acids.

A possible means of detection of HF and not HCl (for differentiation) that was considered was to use HF as a Lewis Type acid catalyst e.g., boron trifluoride, ferric chloride, zinc chloride, iodine, etc. This idea was not acted upon since the HF vapors would always be in the presence of water vapor which would tend to inactivate the HF as concerns its catalytic use.

3.2 SCREENING TESTS

To find a sensitive detector which would also serve as a discriminator between HCl and HF vapors, the following method was used as a qualitative type screening test. The compound under examination was incorporated in 4 wt.% concentration within a liquid crystal compound of 60 wt.% cholesteryl nonanoate and 40 wt.% cholesteryl carbonate. This mixture was dissolved in a solvent of either petroleum ether or petroleum ether/chloroform mixture (using only enough chloroform to effect complete solubility and/or miscibility). A dilution volume ratio of from 7:1 to 10:1 (solvent to liquid crystal-detector system) was used which allowed for film thickness of from 25 μ to 20 μ , respectively. The liquid crystal films were cast on 0.25 mil thick Mylar

film which was stretched on 4.25" brass hoops. The back side of the Mylar was blackened using a dull black paint applied from a spray can (Krylon paint). Application of the liquid crystal-solvent system to the Mylar film was by means of a medicine dropper. Only enough material was applied to the Mylar film to permit even flow to a diameter of 3-4 inches. The solvent(s) was allowed to evaporate, and the liquid crystal film with the incorporated detector was now ready for use.

The method used for sampling HCl and HF was as follows: A 10 cc hypodermic syringe was filled with vapors existing with a bottle of either 36 wt.% of HCl solution or 48 wt.% of HF solution. It was then assumed that the syringe now contained only HCl (or HF) vapors. (Actually, of course, the syringe also contained an appreciable amount of water vapor and air.) This volume was then diluted with air, by repeated emptying to 1 cc and filling with air to 10 cc, until concentrations of approximately a) 100 ppm, b) 10 ppm, and c) 1 ppm were obtained. Gas mixtures of these concentrations were then delivered to the liquid crystal film (prepared as described above) by emptying the syringe approximately 1 in. above the center of the film. In this manner the materials listed in Table 3.2 and Table 3.3 were tested.




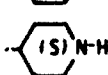
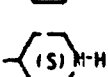
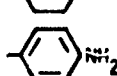
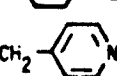
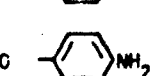
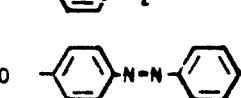
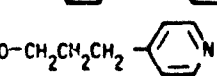
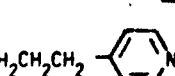


An examination of these two tables provides the screening results concerning reactivity of the listed additives to HCl and HF vapors and to what degree, and whether any specificity existed. Of all the materials tested three appeared to be best for the detection of HCl and HF: oleyl amine, oleyl isonicotinate, and oleyl nicotinate.

Our tests with triphenyl tin chloride as a detector gave no indication of reaction. Since the compound is a known quantitative and qualitative detector of fluoride ions, this was surprising. Other test methods should be tried.

3.3 SENSITIVITY TESTS

Exposure of certain liquid crystal matrices to HCl levels of 1 - 10 parts per million (ppm) was known to produce a response. In order to measure the sensitivity accurately, a means of exposing the

Table 3.2 - Materials Prepared for the Detection of HCl and HF.

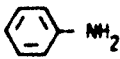

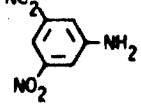

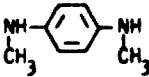
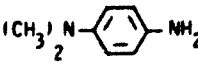
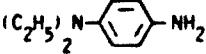
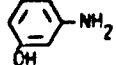
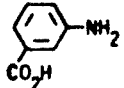

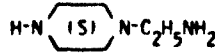
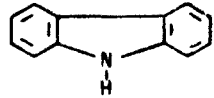
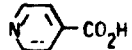
Name	Structure	Physical Property	Results *
Cholesteryl isonicotinate	$C_{27}H_{45}O-C(=O)-$ 	mp 167.4° - 167.7°C	G
Oleyl isonicotinate	$C_{18}H_{35}O-C(=O)-$ 	bp 178°/0.04 mm	AKN
Oleyl nicotinate	$C_{18}H_{35}O-C(=O)-$ 	bp 191°/0.07 mm	BKN
Cholesteryl isonipeccatoate (not completely purified)	$C_{27}H_{45}O-C(=O)-$ 		LG
Oleyl isonipeccatoate	$C_{18}H_{35}O-C(=O)-$ 	bp 130°/0.1 mm	FO
Cholesteryl p-aminobenzoate	$C_{27}H_{45}O-C(=O)-$ 	mp 238-239°C	LG
Cholesteryl 4-pyridylacetate (not completely purified)	$C_{27}H_{45}O-C(=O)-CH_2-$ 		G
Cholesteryl p-aminophenyl carbonate	$C_{27}H_{45}O-C(=O)-O-$ 	mp 223°C	G
Cholesteryl p-phenylazophenyl carbonate	$C_{27}H_{45}O-C(=O)-O-$ 	mp 166° - 167.9°C	G
Cholesteryl 3-(4-pyridyl) propylcarbonate (not completely purified)	$C_{27}H_{45}O-C(=O)-O-CH_2CH_2CH_2-$ 		G
Cholesteryl 3-(4-pyridyl) propyl ether (not completely purified)	$C_{27}H_{45}O-CH_2CH_2CH_2-$ 		G
N-cholesteryl aniline	$C_{27}H_{45}-N(H)-$ 	mp 189° - 190°C	G
N-cholesteryl-N-phenylhydrazine	$C_{27}H_{45}-N(NH_2)-$ 	mp 198° - 199°C	G
Oleyl amine	$C_{18}H_{35}-NH_2$	bp 126°/0.06 mm	AN

★

- A. Strong response to both HCl and HF - does not fade on heating
- B. Strong response to HCl - weak response to HF
- C. Strong response to HCl - no response to HF
- E. Weak response to both HCl and HF
- F. Weak response to HCl - no response to HF
- G. No response to either HCl or HF

- H. Fuming
- I. Response fades on heating
- K. Response is permanent at room temperature
- L. Very limited solubility in liquid crystal matrix
- M. Additive too volatile
- N. Limited differentiation by appearance
- O. Temporary change - slowly disappears at room temperature

Table 3.3 - Additives Tested for the Detection of HCl and HF.

Name	Structure	Results*
Aniline		M
p-Nitroaniline		LG
3,5-Dinitroaniline		L
p-Phenylene diamine		EI
N,N'-Dimethyl-p-phenylene diamine		BH
N,N-Dimethyl-p-phenylene diamine		BNK
N,N-Diethyl-p-phenylene diamine		BHK
m-Aminophenol		F
m-Aminobenzoic acid		LG
Pyrrolidine		AHI
N-Aminoethyl piperazine		F
Carbazole		G
Isonicotinic acid		L

* See Table 3.2 for definitions

Table 3.3 - Continued

Name	Structure	Results*
Isonicotinic acid hydrazide		L
p-Azoxyanisole		L
L-1 Tyrosine		L
p-Diamino diphenyl sulfide**		AN
p-Diaminodiphenyl oxide**		LF
p-Aminoacetanilide		LG
3,4-Diaminobenzanilide		LG
o-Methylbenzyltrimethylamine		EH
Phenylethanol amine		BHI
Phenyl ethyl ethanolamine		EI
Tribenzylamine		AN
1,5-Diaminonaphthalene		L
Di-n-butyl-3-aminopropylamine		AH
Hexadecylamine		A
Pyridine		M
Piperidine		AHI

* See Table 3.2 for definitions

** Dimethyl acetamide solvent needed to dissolve these materials into mixture

entire surface uniformly to a known concentration of gas for a prescribed interval was necessary. This method* used the partial pressure data² for aqueous solutions of HCl. It was found that pressures of .00024 to .0067 mm HCl could be obtained from 4% to 10% aqueous solutions at 20° - 25°C; see Figures 3.1, 3.2 and 3.3. Since the partial pressure of a gas divided by the total atmospheric pressure yields directly the mole fraction present, the calculation of the amount of HCl in the vapor in ppm was possible³.

Variations in temperature affected this partial pressure; therefore, the mole fraction present could be controlled easily by varying either the temperature or concentration of the solution, although during specific exposure periods both had to be held constant. In practice, the concentration was determined accurately and the temperature was measured during the exposure of the film. From these data and interpolation curves, concentration could then be readily determined.

The equipment used for the detection of HCl consisted of a desiccator, thermometer, volumetric flasks, burets, standard base solution (0.500N NaOH), and miscellaneous glassware necessary for the liquid crystal handling and exposure. The apparatus was set up as illustrated in Figure 3.4.

Liquid crystal materials were prepared which consisted of 60 parts (by weight) of cholesteryl nonanoate and 40 parts (by weight) of cholesteryl oleyl carbonate to which 4% by weight (based on the 60/40 mix) of various detectors were added to make the detector solutions. To keep the cholesteryl nonanoate-cholesteryl oleyl carbonate ratio constant, a 10 gram batch of the mixture was diluted with petroleum ether to 100 ml, then 10 ml aliquots were transferred to each of seven 30 ml sample bottles. Each bottle then contained one gram of the

*RADC suggested this method of obtaining atmospheres having very low contamination levels of known concentration.

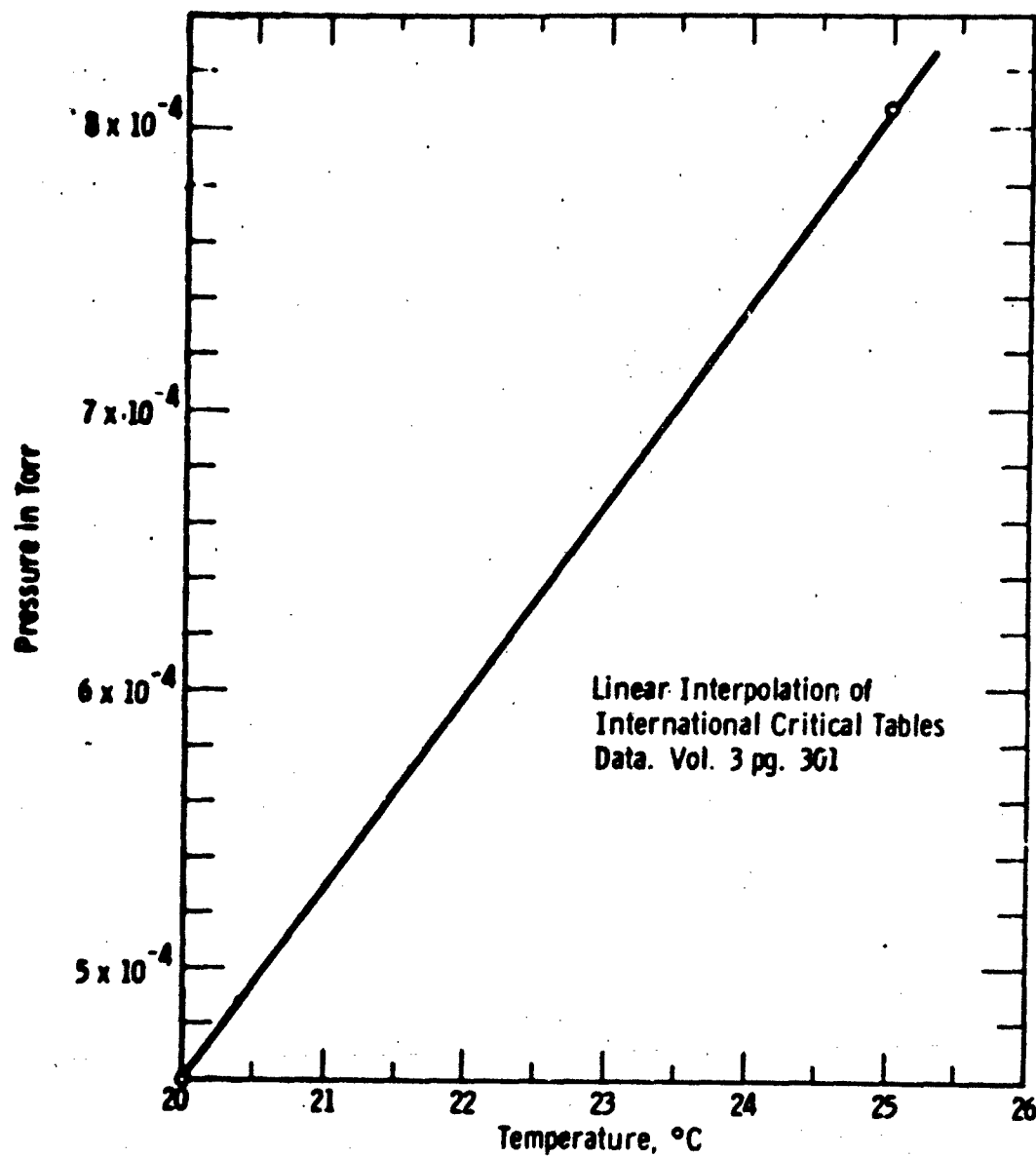


Figure 3.1 - Vapor pressure of 4.84% aqueous solution of HCl (1.614 N).

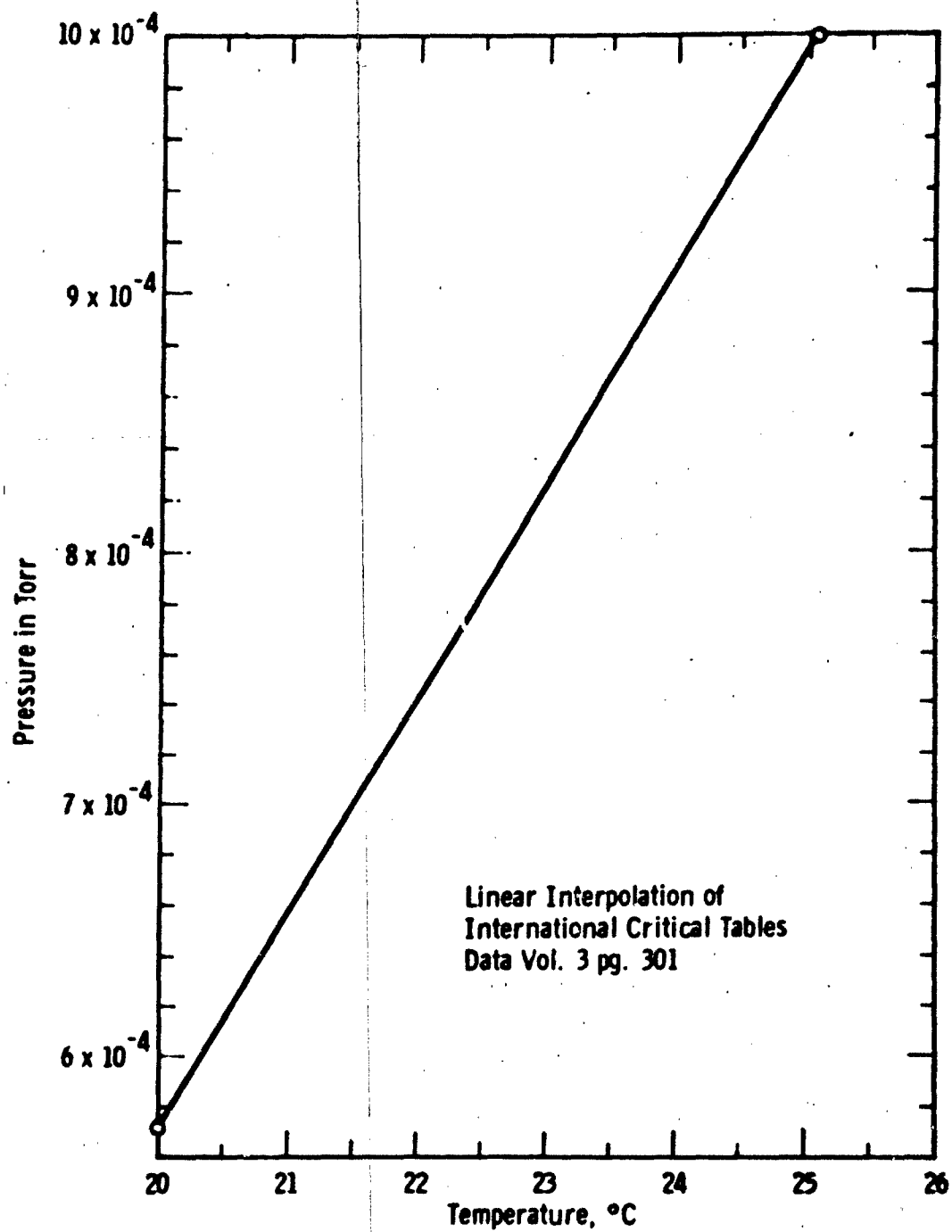


Figure 3.2 - Vapor pressure of 5.28% aqueous solution of HCl (1.760 N).

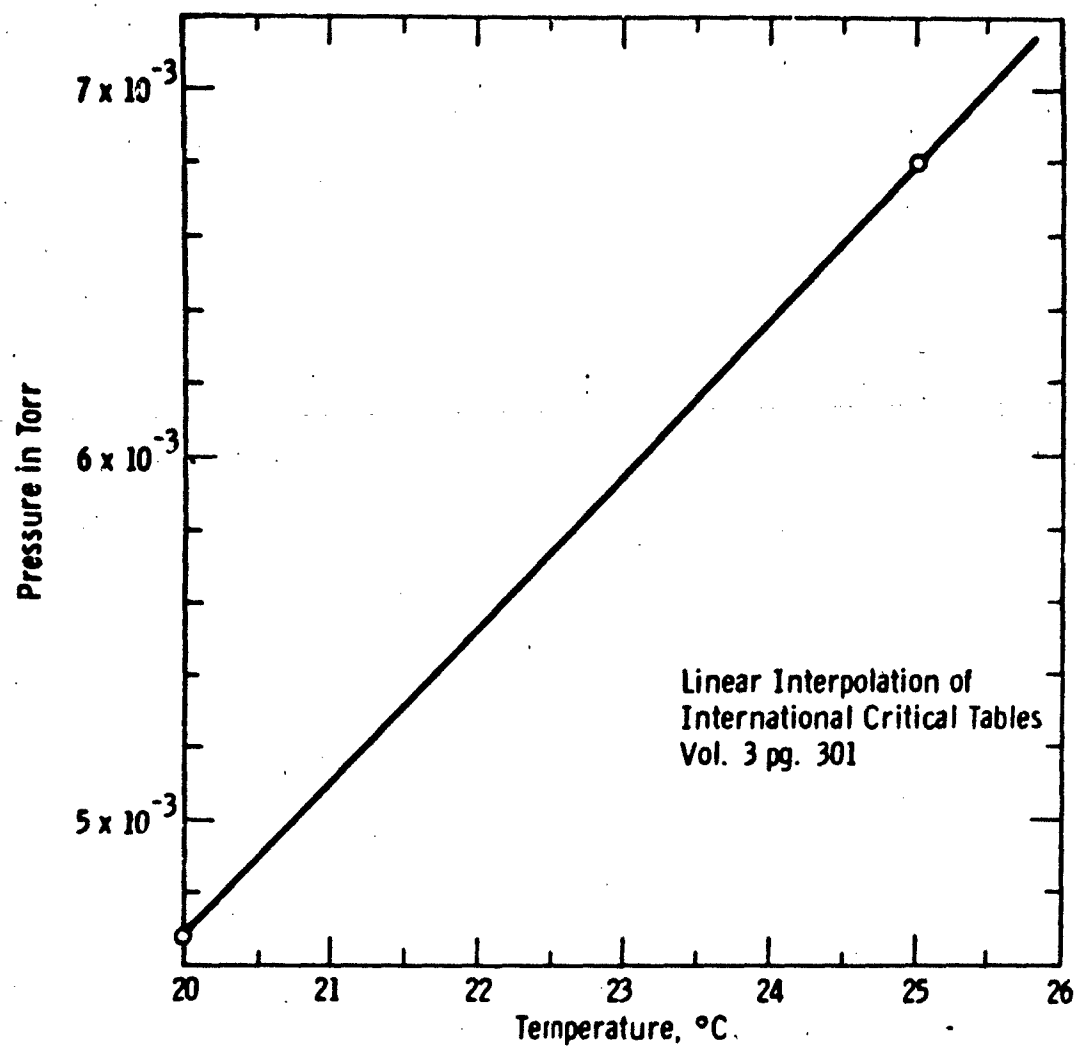


Figure 3.3 - Vapor pressure of 10.3% aqueous solution of HCl (3.433 N).

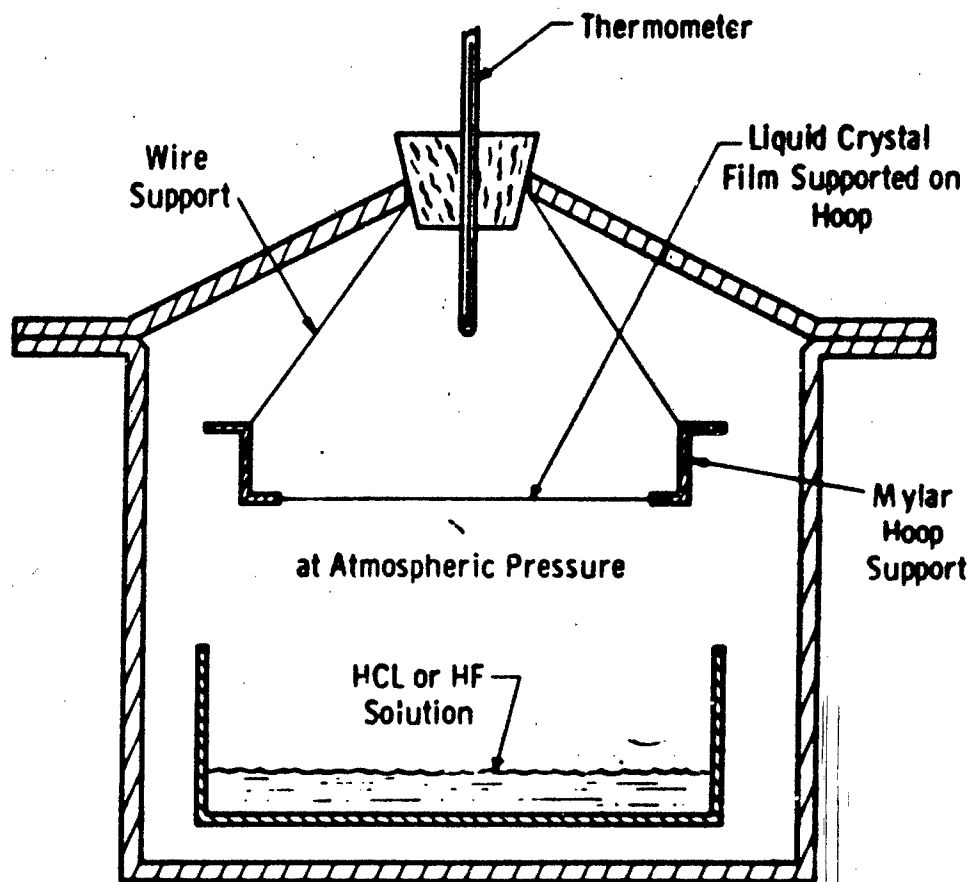


Figure 3.4 - Apparatus for exposure of a liquid crystal film to HCl and HF vapors.

60/40 weight mixture of cholesteryl nonanoate-cholesteryl oleyl carbonate. Forty milligrams of the appropriate detector were added, and each solution was then stirred to give 3.85% by solids weight of detector. These solutions are nominally referred to as 4% solutions.

For the measurement of HCl detection, solutions of 1.614 N (5.9% by weight), 1.760 N (6.4% by weight), and 3.433 N (12.5% by weight) HCl were made, and titrated to a phenolphthalein end point as a check. Before exposure the appropriate solution was placed in the desiccator, and after allowing time for the atmosphere to reach equilibrium, the top of the desiccator was removed carefully to insert the liquid crystal film. The film was suspended for a predetermined time, usually 15 or 30 minutes, and then removed. The temperature vs wavelength characteristics of this film were measured before and after exposure (on the apparatus described in Figure 3.4), and the change or shift in temperature recorded. Oleyl amine, oleyl isonicotinate, and oleyl nicotinate detectors were used (incorporating them in the 60/40 cholesteryl nonanoate/cholesteryl oleyl carbonate matrix) and tested as described. The temperature response (in degrees Centigrade) versus wavelength of reflected light (in Angstroms) was plotted for each of the films before and after 15 min and/or 30 min exposures to 1 and/or 10 ppm of contaminant. The magnitude of shift in color temperature with concentration of contaminant is a measure of the sensitivity.

For the HF solutions, vapor pressure data similar to that available for HCl solutions were scarce. Since the solutions of HCl which gave 1 to 10 ppm of HCl in the vapor above the solution could be determined easily², it was decided to use this same technique for the approximation of partial pressures of HF gas above aqueous solutions of HF. From a qualitative and semiquantitative work (the hypodermic syringe technique of dilution) it was noted that comparable dilution of aqueous HCl and HF vapors gave very similar results with oleyl amine as the detector in a liquid crystal matrix of cholesteryl oleyl carbonate and cholesteryl nonanoate. Therefore, since the HF molecule is considerably lighter in weight than the HCl molecule (20.01 vs 36.47), the HF solutions that were made up vary from 1% to 10% by

weight as compared to the HCl solutions which varied from (6% to 12.5%). In this manner, aqueous solutions of HF were prepared which provided approximately 1 to 10 ppm of HF in the vapor above the solution based on the aqueous HCl solution-vapor pressure data obtainable from tables².

It will be noted that some of the detecting materials which react with HCl and HF vapors may also react with the oxides of nitrogen. Fortunately the effects are opposite; that is, the effect of oxides of nitrogen is to depress the temperature range of the liquid crystal film while the effect of the halogen acids is to raise it.

When performing sensitivity measurements, care was taken not to use chloroform as part of the liquid crystal-detector solvent system. It is known that chloroform is light sensitive and one of the products of degradation is HCl which would interfere with the test.

In performing the actual sensitivity measurements, temperature vs wavelength tests were first made using the oleyl amine "doped" liquid crystal system to determine the film to film variation. Results showed that each individual film had to be treated individually. All the data were normalized to account for changes during preparation, or variations of trace amounts of contaminants in the atmosphere at the different times that the films were cast. Once made, however, the films fluctuate very little while maintaining their sensitivity to trace contaminants.

Of all the materials tested, the oleyl amine proved to be the most sensitive detector. A 4% solution of oleyl amine in the 60/40 cholesteryl nonanoate-cholesteryl oleyl carbonate produced a twelve degree rise in the operating temperature of the liquid crystal matrix after having been exposed for 15 minutes to 8 ppm. Another film was exposed to 1 ppm for 15 minutes and it showed changes of approximately a degree in the same direction (refer to Table 3.4 and Figure 3.5). These results correspond to a sensitivity of roughly 1 to 1.5°C/ppm. A sample left 18 hours in an unsealed plastic container exhibited a color transition temperature shift of only 0.3 degree.

Table 3.4 - Temperature Shift (°C) of 4% Oleyl Amine in 60/40 Cholesterol Nonanoate/Cholesteryl Oleyl Carbonate Exposed to HCl

<u>Color</u>	<u>Wave-length (Å)</u>	<u>Un-exposed temp. (°C)</u>	<u>Un-exposed (aged 18 hr)</u>	<u>15 min, 0.9 ppm</u>	<u>16 hr, 1 ppm</u>	<u>15 min, 8 ppm</u>
UV	3888	30.81	+ .29	+ .76	+4.2	+12.1
Blue	4471	28.83	+ .46	+ .83	--	--
Green	5015	28.20	--	--	+4.5	--
Yellow	5875	27.68	+ .51	+1.00	+4.7	+12.0
Red	6560	27.29	+ .59	+1.10	--	+12.1

Table 3.5 - Temperature Shift (°C) of 4% Oleyl Amine in 60/40 Cholesterol Nonanoate/Cholesteryl Oleyl Carbonate Exposed 15 Min to HF Water

<u>Color</u>	<u>Wave-length (Å)</u>	<u>Un-exposed temp. (°C)</u>	<u>1 wt.% HF (1 ppm)</u>	<u>10 wt.% HF (8 ppm)</u>
UV	3888	30.81	+2.14	+13.4
Blue	4471	28.83	+1.58	+13.5
Green	5015	28.20	--	+13.5
Yellow	5875	27.68	+1.70	+13.4
Red	6560	27.29	+1.73	+13.4

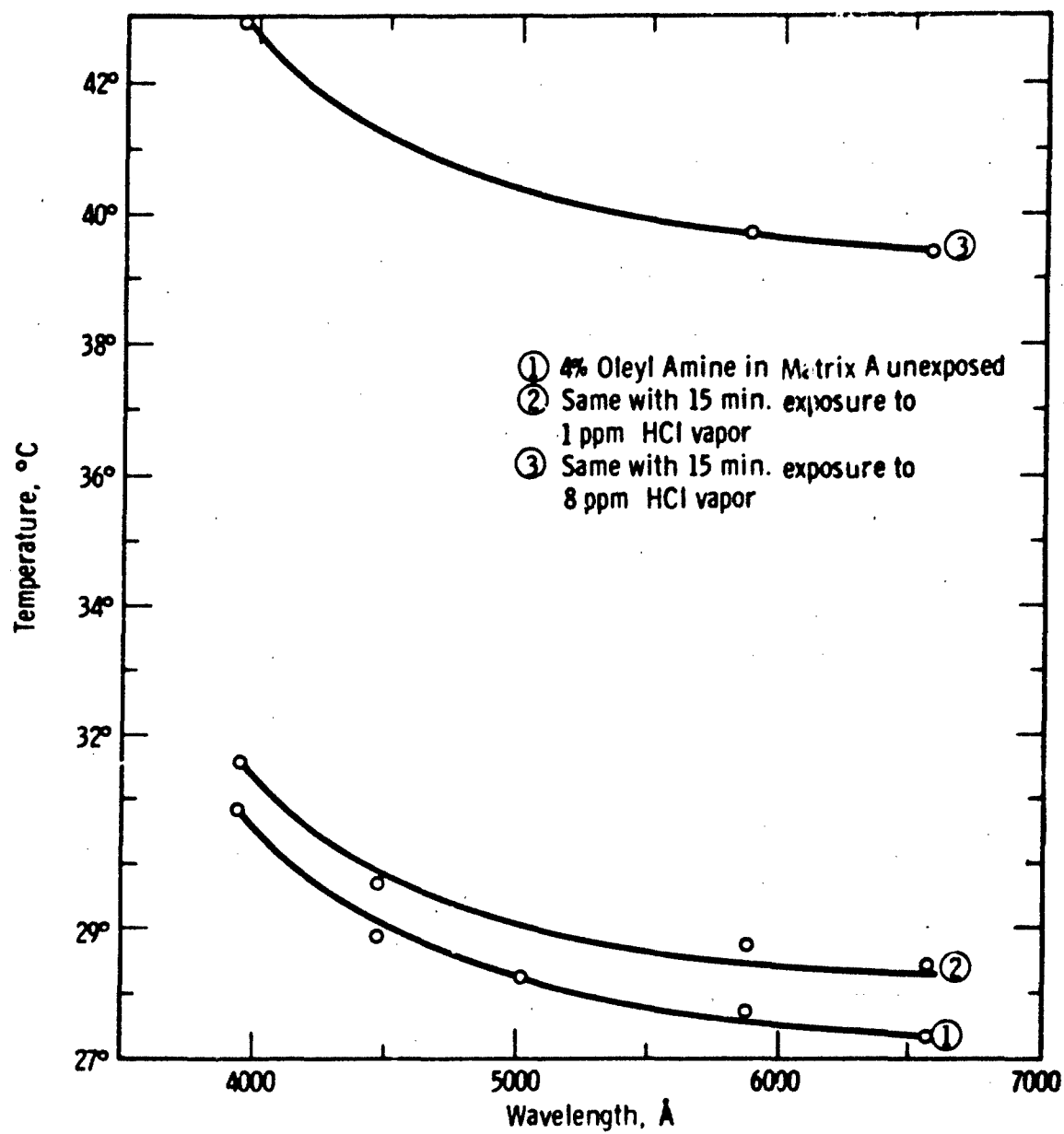


Figure 3.5 - Effect of 15 min exposure by HCl on Matrix A + 4% Oleyl Amine.

Referring to Table 3.5 and Figure 3.6, the detection of HF with 4% oleyl amine, exceptional sensitivity was noted. After 15 minute exposure to 10% HF the color temperature of the film was raised approximately 13.5°C, while the color temperature rise noted for 1% HF was about 1.5-2°C.

In the screening tests, oleyl nicotinate appeared to be a very sensitive detector, i.e., exposure to either HCl or HF seemed to produce a large shift in the operating temperature. When tested under controlled conditions, however, the effect on films containing oleyl nicotinate did not exceed a 0.5°C shift. Referring to Table 3.6, there is very little change noted between 15 minute exposures to 1 ppm or 8 ppm or HCl vapor. In the case of HF (Table 3.7) an anomaly can be seen. The oleyl nicotinate reacted with HF in a manner such that a greater shift in transition temperature is noted with an exposure of 15 minutes to 1% HF than a 15 minute exposure to 10% HF. In both instances, however, the shift is rather small so it may mean that in both cases the detector had become saturated.

Table 3.8 shows the results of testing HCl with oleyl isonicotinate as the detector. When a film is exposed to 1 ppm HCl vapor for 15 minutes, a lowering of the operating temperature results; however, if a similar film is exposed to 8 ppm for 15 minutes the color temperature is raised. When the same material was exposed to HF, unusual results were obtained as shown in Table 3.9. The temperature shift in the U.V. was negative for 1 ppm concentrations but positive for 8 ppm. The temperature shift in the yellow and red was positive after 15 minutes exposure, but negative after 30 minutes. With 8 ppm and 17 minutes exposure the temperature shift was positive for all wave lengths.

3.4 CONCLUSIONS

This study has conclusively shown that a selective test for the detection of HCl and HF at 1 ppm is possible. Quantitative

Table 3.6 - Detection of HCl with 4% Normalized Oleyl Nicotinate in
60/40 Cholesteryl Nonanoate/Cholesteryl Oleyl Carbonate

<u>Color Reflected</u>	<u>λ(A)</u>	<u>Temperature Unexposed ($^{\circ}$C)</u>	<u>Change in temp. ($^{\circ}$C)</u>	
			<u>After 15 min, 0.9 ppm</u>	<u>After 15 min, 8 ppm</u>
UV	3888	28.39	+.24	+.02
Blue	4471	26.10	+.17	-
Green	5015	25.25	+.18	-
Yellow	5875	24.46	+.20	+.44
Red	6560	24.02	+.15	+.49

Table 3.7 - Detection of HF with 4% Normalized Oleyl Nicotinate in
60/40 Cholesteryl Nonanoate/Cholesteryl Oleyl Carbonate

<u>Color Reflected</u>	<u>λ(A)</u>	<u>Temperature Unexposed ($^{\circ}$C)</u>	<u>Change in temp. ($^{\circ}$C)</u>	
			<u>After 15 min, 1 wt. %</u>	<u>After 15 min, 10 wt. %</u>
UV	3888	28.39	+.24	+.20
Blue	4471	26.10	+.17	-
Green	5015	25.25		-
Yellow	5875	24.46	+.34	+.24
Red	6560	24.02	+.34	+.20

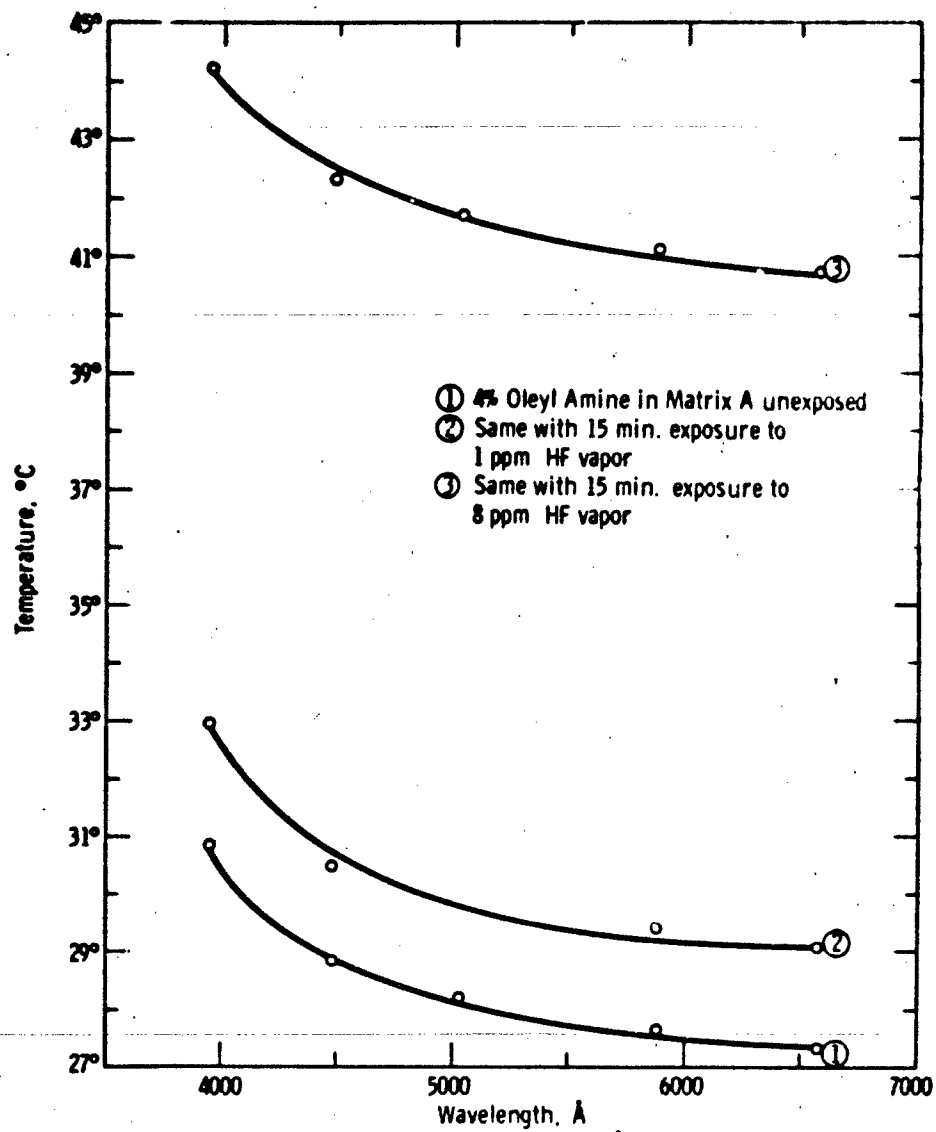


Figure 3.6 - Effect of 15 min exposure by HF on Matrix A + 4% Oleyl Amine.

Table 3.8 - Detection of HCl with 4% Oleyl Isonicotinate in 60/40
Cholesteryl Nonanoate/Cholesteryl Oleyl Carbonate

<u>Color Reflected</u>	<u>$\lambda(A)$</u>	<u>Temperature, Unexposed</u>	<u>Change in Temp. (15 min exposure)</u>	
			<u>0.9 ppm</u>	<u>8 ppm</u>
UV	3888	29.98°C	-.13°C	+.15°C
Blue	4471	27.81	-.17	+.19
Green	5015	27.00	-.12	
Yellow	5875	26.29	-.12	+.03
Red	6560	25.90	-.15	+.00

Table 3.9 - Detection of HF with 4% Oleyl Isonicotinate in 60/40
Cholesteryl Nonanoate/Cholesteryl Oleyl Carbonate

<u>Color Reflected</u>	<u>$\lambda(A)$</u>	<u>Temperature, Unexposed*</u>	<u>Change in Temperature</u>		
			<u>15 min 1% by Wt (1 ppm)</u>	<u>30 min 1% by Wt (1 ppm)</u>	<u>17 min 10% by Wt (8 ppm)</u>
UV	3888	29.98°C	-.05°C	-.24°C	+.218°C
Blue	4471	27.81	-	-.12	+.17
Green	5015	27.00	-	-.17	-
Yellow	5875	26.29	+.07	-.15	+.24
Red	6560	25.90	+.07	-.17	+.24

*After normalization

results have been shown for gas concentrations between 1 and 10 ppm. Success in separate identification of HCl or HF was not obtained. From our studies it appears doubtful that a simple liquid crystal test can be made for the separation of HCl and HF based on acid-base strength.

3.5 REFERENCES

1. Organic Analytical Reagents, Vol. IV, F.J. Welcher, D. Van Nostrand Co., Inc., New York, 1948, p 330.
2. International Critical Tables, Vol. 3, p 301, 1926.
3. Principles of Physical Chemistry, S.H. Maron, C.F. Prutton, Macmillian Co., N.Y., 1958, p 16.

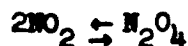
4. DETECTION OF TRACE NITROGEN OXIDES

4.1 INTRODUCTION AND THEORY

A literature survey was made to find possible chemical interactions between organic compounds and the five oxides of nitrogen, i.e., nitrous oxide (N_2O), nitric oxide (NO), nitrogen trioxide (N_2O_3), nitrogen pentoxide (N_2O_5), and nitrogen dioxide or tetroxide [$2(NO_2)$ or N_2O_4]. The purpose was to find reactions which would occur rapidly between the oxides and chemical compounds. This type of reaction would disturb the geometric arrangement of the liquid crystal containing various concentrations of this compound and, therefore, cause a visible, permanent change of color or other perceivable physical change.

No evidence was found that N_2O , nitrous oxide, reacts with any compound at room temperature or at relatively low temperatures (1,2). However, several papers and reviews (3,4,5,6,7,8,9,10) deal with the effect of N_2O_4 and of other oxidizing agents on various types of organic compounds, mainly unsaturated.

Some of the literature (11) indicates that oxides of nitrogen undergo many reactions in the atmosphere, for example with oxygen or with moisture. Almost instantaneous equilibrium is claimed for the reaction



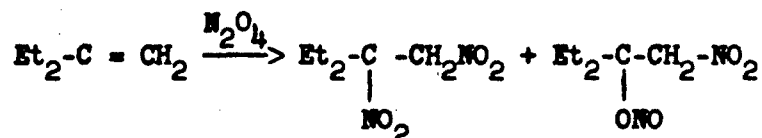
but, at concentrations of the order of fractions of part per million, the equilibrium actually lies far to the left. In general, the distribution of the various nitrogen oxides in air is said to be a function of their respective concentrations, with nitrogen oxide in either form being one of the most important, together with nitric acid. These statements, of course, must be taken in the light of the fact that the

distributions and equilibrium mentioned in this paper are part of a study of nitrogen oxides in a particularly contaminated atmosphere, and may not always hold. In any case, this investigation was focused upon nitrogen dioxide, although some data on nitric acid also appear in the report.

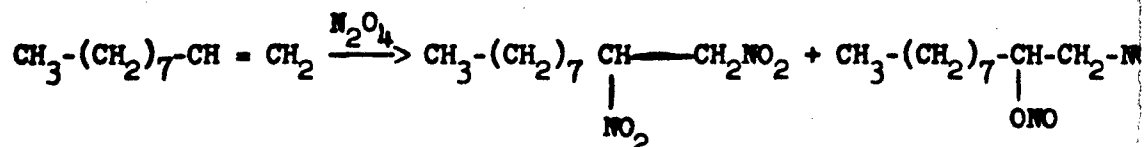
Riebsomer (3) made an extensive survey of the reactions of N_2O_4 with organic compounds. A very large number of chemical compounds were nitrated by N_2O_4 , some with interesting results. For example, some organometallic compounds react vigorously giving the corresponding diazonium nitrates $RN = NNO_3$.

Aromatic hydrocarbons can be nitrated rapidly with N_2O_4 using $AlCl_3$ as a catalyst. In general, double bonds are saturated, and in one case maleic acid (cis) was transformed into its geometric isomer, fumaric acid (trans) (10). Riebsomer found that N_2O_4 is not a better nitrating agent than HNO_3 , but that it is useful under certain circumstances in additions to compounds containing double bonds and as an oxidizing agent.

Porter and Wood (6) examined the reactions of olefins with N_2O_4 in order to characterize them and to determine the position of the double bond. Dec-1-ene and 2-ethylbut-1-ene (ten and four chain carbon atoms respectively, terminal double bond) add the tetroxide to give 1,2-addition, e.g.,



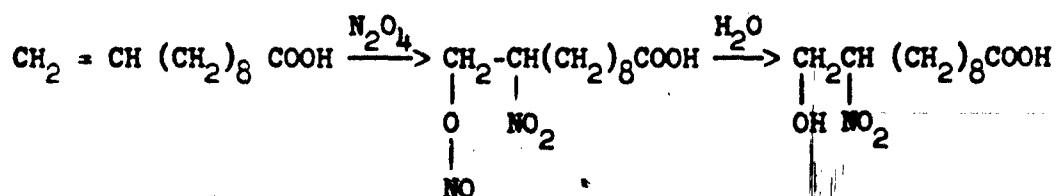
and



The nitrite groups (-ONO) so obtained can be partially hydrolyzed, and the nitro groups (-NO₂) can be reduced to the corresponding amine by

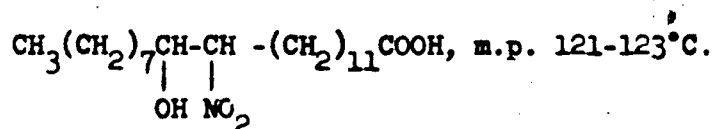
common procedures. This type of reaction may be useful for the detection of nitrogen tetroxide. However, it is claimed that the greater the molecular weight of the unsaturated olefin with terminal double bond, the less rapid the reaction with N_2O_4 .

S.V. Vasil'ev (7) studied the effect of N_2O_4 on undecylenic acid in ether solutions. He found that under the action of either gaseous or liquid nitrogen tetroxide, undecylenic acid first gives a nitrosite, which then changes into crystalline nitroxyundecylenic acid:



The crystalline nitroxyundecylenic acid (m.p. 121-122°C) precipitates out, thus providing a drastic change in the chemical system involved.

In another paper S.V. Vasil'ev (8) investigates the effect of N_2O_4 on erucic acid $CH_3(CH_2)_7CH=CH(CH_2)_{11}COOH$. Here the final product was the crystalline nitroxybehenic acid (behenic acid being the C_{22} saturated fatty acid):



Under the conditions employed by the author, no double bond shift was observed, but only N_2O_4 addition followed by partial hydroxylation.

While oxides of nitrogen have been used for a long time to isomerize fatty acids, little is known about the efficiency of each oxide. N.A. Kahn (1) investigated the effect of N_2O , NO and N_2O_4 on methyl oleate and methyl linolenate, and followed the change of the double bond (isolated trans double bond = 10.32u) and the appearance of nitrogen derivatives (6.11 and 6.44u) by means of IR and UV analysis. He found that N_2O_4 was the only oxide which brought about both nitration and isomerization, generally accompanied by an exotherm, which

was high enough to polymerize methyl linolenate. Neither of the other oxides caused isomerization. The author proposes a mechanism for the conversion of cis- to trans- modifications of the unsaturated higher fatty acid esters by N_2O_4 .

Both the isomeric change and polymerization caused by the exothermic reaction between N_2O_4 and the linolenate ester may be of use in the detection of N_2O_4 . A paper by K. Fuse and B. Tanamushi (9) describes the conversion of oleic acid to elaidic acid by the action of oxides of nitrogen. They claim almost complete conversion on allowing oleic acid to absorb N_2O_4 for 3 and 4 minutes at 20°C. However, the authors made no attempt either to differentiate between the various oxides of nitrogen (which they obtained by the action of conc. HNO_3 on copper) or to analyze the reaction products. They assumed that the amount of oxides needed to catalyze the conversion of oleic acid into elaidic acid is approximately 1/10 of that needed for the addition reaction.

The question of whether one is dealing with NO_2 or N_2O_4 , depending on the gas pressure and on its concentration in air, was not resolved. Attempts to have the commercial nitrogen dioxide used in this work analyzed by mass-spectrometric methods gave inconclusive results. Thus one is obliged to deal with the nitrogen oxide in question as "nitrogen dioxide", keeping in mind that probably the used nitrogen dioxide is mostly NO_2 .

4.2 SCREENING TESTS

Confronted with a multitude of compounds containing unsaturation which might react with the oxides of nitrogen, several were chosen for screening tests, mainly on the basis of literature reference and of previous experience in other chemical fields. They were either added to a common matrix or were reacted into a matrix to obtain a presumably more homogeneous reactive compound. See legend for Figures 4.1 and 4.2.

4.2.1 Methods and Apparatus

The liquid crystal materials were each dissolved in a solvent consisting of 3 parts petroleum ether and 1 part chloroform. A solids content of 10 or 15% was found to give the desired thickness (20 to 25 μ). Screening tests were conducted using brass hoops (4.25 inch in diameter) covered with thin blackened mylar sheeting, on which the detecting liquid crystal solution to be examined was spread thinly and from which the solvent was allowed to evaporate slowly at room temperature. The test set-up consisted of a thermoelectric element block with attendant electronic auxiliaries; this element, whose testing metal surface was about 1.5 x 1.5 inches, was placed over a large copper block which acted as a heat sink, and the whole was immersed in water. The hoop to be tested was placed on the thermoelectric metal block (into which a thermometer had been inserted). A glass pane was placed on the hoop over the spread-out liquid crystal to avoid temperature-vitiating air currents and to contain the contaminant gas. The temperature of the thermoelectric block in contact with the mylar sustaining the liquid crystal was increased or decreased as desired, usually at a rate of 1.5°C per minute, while color changes or shifts were noted as they occurred as a function of the temperature. Exposure of the sample to the gas was attained either by directing the gas flow right onto the liquid crystal for undiluted exposure, or by removing a sample of the gas from the tank with a calibrated syringe, and then by diluting this quantity repeatedly with a known amount of air to obtain approximately the dilution desired. Subsequently a known amount of this diluted gas was injected under the glass plate lying on the liquid crystal hoop and was allowed to react with the crystal for a predetermined length of time.

In general, temperature-color shift readings were taken before and after exposure. Note was taken not only of the temperatures at which color appeared and disappeared, but also of

the behavior of the crystal. A way to plot or record the results obtained is shown by Figures 4.1 and 4.2 where the bargraphs or vertical lines indicate the temperature range covered by the whole color shift for any particular matrix or combination of gas detectors investigated. The length of each bar is an indication of sharpness of the detection reaction, that is, the longer the bar the longer the time during which a complete color shift takes place. All the experiments were run at least in duplicate and each of them was carried out observing the color shift both with rising and lowering temperatures which reproduced themselves with 0.5 degree Centigrade. Since this was intended to be a rough, screening type of testing, this accuracy was thought sufficient.

4.2.2 Materials

On the basis of previous considerations, liquid crystal detectors for nitrogen dioxide were chosen among compounds containing different degrees of unsaturation. The technique consisted of testing either a liquid crystal matrix whose inherent structure contained unsaturation or one to which unsaturated compounds were added.

The detectors examined and reported in Figure 4.1 are given below. All ratios and percentages are by weight.

- A. 60:40 ratio of cholesteryl nonanoate and cholesteryl oleyl carbonate (one double bond in the oleyl portion)
- B. 40:40:20 ratio of nonylphenyl carbonate, cholesteryl nonanoate and cholesteryl benzoate (this matrix contained no unsaturation outside of that in the cholesteryl and phenyl portions and was used mainly as a basic matrix)
- C. Cholesteryl cinnamate (one double bond in the cinnamate)
- D. Cholesteryl 10 undecenoate (one double bond in the undecenoate)
- E. Matrix A plus 1% oleic acid (one double bond in the oleic fraction)
- F. Matrix B plus 2% triolein (three double bonds, a glyceride)
- G. Matrix B plus 2% cinnamyl alcohol (one double bond in the alcohol fraction)

cal
d.
h
ed
ent.

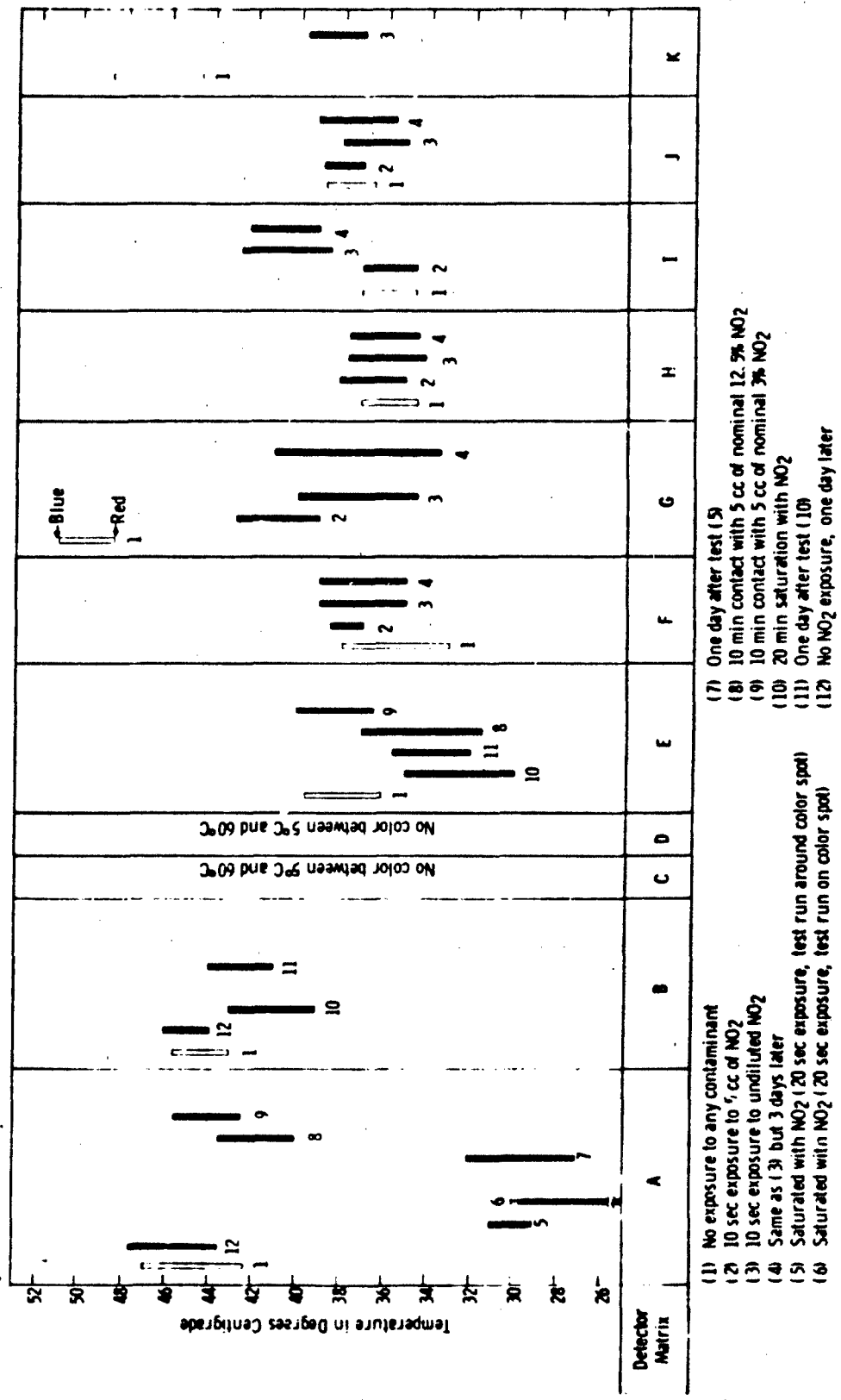


Figure 4.1 -- Screening test to determine the best matrix for NO₂ detection.

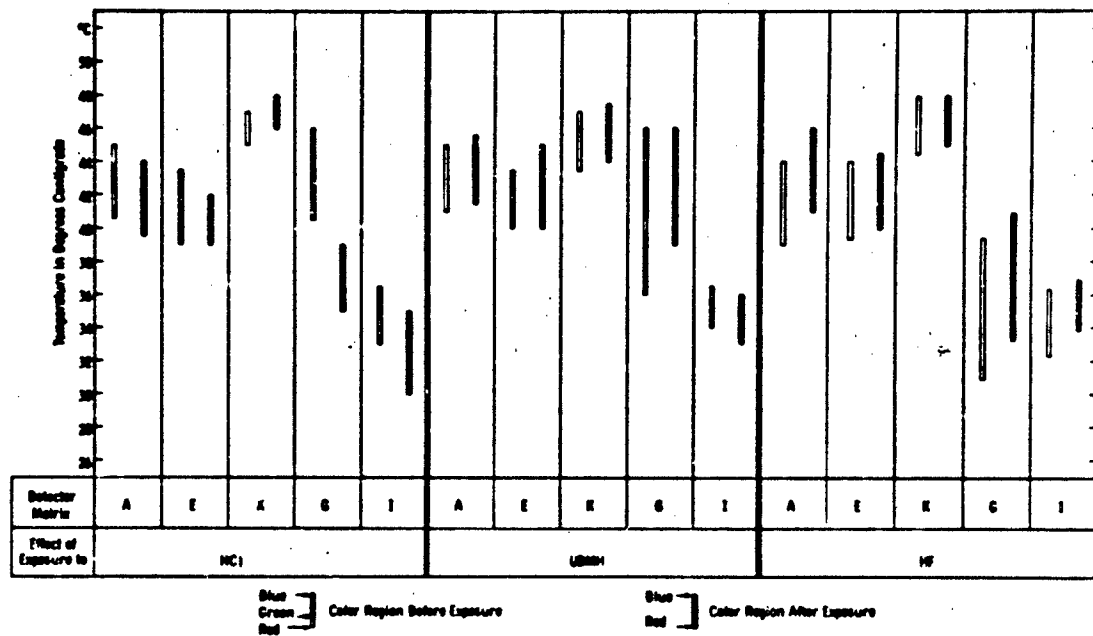


Figure 4.2 - Effects of exposing selected NO₂ detectors to HCl, UDMH, and HF.

- H. Matrix B plus 2% methyl oleate (one double bond in oleate fraction)
- I. Matrix B plus 2% methyl linoleate (2 double bonds in linoleate fraction)
- J. Matrix B plus 2% methyl linolenate (3 double bonds in linolenate fraction)
- K. Matrix B plus 2% trans-cinnamaldehyde (one double bond in cinnamaldehyde fraction)

It must be noted that this method of indicating matrices (by themselves or with added detecting agents) with capital letters was used throughout this phase of the work. Each letter, except the two (A and B) indicating basic matrices, merely tells the nature of the detecting agent added onto a basic matrix; each important variation in concentration is spelled out in the text.

Test hoops coated with a thin layer of the above detectors were treated under the conditions shown in the legend of Figure 4.1, as indicated by the number under each color shift line. A detecting matrix was considered to be reactive if the temperature range of the color shift line before and after exposure to gas contamination was unequivalent.

4.2.3 Results

Of the eleven detecting matrices reported in Figure 4.1, the following gave indication of usefulness in detecting nitrogen dioxide: A (60:40 cholesteryl nonanoate plus cholesteryl oleyl-carbonate); E (matrix A + 1% oleic acid); G (matrix B plus 2% cinnamyl alcohol); I (matrix B + 2% methyl linoleate); and K (matrix B + 2% trans-cinnamaldehyde).

It is interesting to note that matrix H, with 2% methyl oleate (one double bond in the oleate fraction) and matrix J, with 2% methyl linolenate (three double bonds in the linolenate fraction) did not show much sign of reactivity while matrix I with 2% methyl linoleate (two double bonds in the linoleate fraction) did show unmistakably a

reaction on exposure to nitrogen dioxide. A possible explanation might be that one double bond does not react to a sufficient degree of liquid crystal perturbation, while three double bonds (as found in very reactive drying oils) may be responsible for a much too drastic dimerization or polymerization reaction which might immobilize the liquid crystal structure. On the other hand, in the case of reactive matrix A, the unsaturated oleic portion is an integral part of the molecule and it appears in sufficient concentration to yield a sensitive reaction.

It is also obvious from Figure 4.1 that contaminant concentration is directly responsible for the degree of response in the reactant materials and that, generally, the effect of the reaction between nitrogen dioxide and any of the relatively successful detecting matrices will last at least one day and usually three days.

The matrices containing cinnamyl alcohol and cinnamaldehyde as additives seemed to offer the most promising results as shown by the large difference in color shift temperature ranges before and after exposure.

The same technique for testing contaminant effect on detecting liquid crystals was used to determine whether the above five candidates were selective in the detection of nitrogen dioxide. Thus, test hoops were spread with matrices A, E, K, G and I as described previously, and were subjected to the effect of contaminant HCl, HF and UDMH (unsymmetrical dimethyl hydrazine) as follows:

In the case of HCl, the sample was exposed to concentrated HCl gas for 10 minutes as previously described for nitrogen dioxide. In the cases of HF and UDMH, the test hoops were exposed for 20 minutes to undiluted fumes of HF and UDMH. The temperature bars in Table 4.1, where the reactivity of five liquid crystal matrices to nitrogen dioxide, hydrochloric acid, unsymmetrical dimethylhydrazine and hydrofluoric acid are indicated in a semiquantitative manner. The contaminant concentrations in all cases reported in Figure 4.2 and Table 4.1 are considered to be of the same order of magnitude.

Table 4.1 - Reactivity of Five Liquid Crystal Matrices to Four Gases.

Matrix	Reactivity to:			
	NO ₂	HCl	UDMH	HF
A	Strong	None	None	Slight
E	Moderate	None	None	None
K	Strong	None	None	None
G	Strong	Moderate	None	Slight
I	Moderate	Slight	None	None

Thus, all the selected nitrogen dioxide indicators, except perhaps the one containing cinnamyl alcohol, are shown to be reasonably selective toward nitrogen dioxide gas.

4.3 SENSITIVITY TESTS

The work and the preliminary results reported above provided us with a workable body of information and with a restricted group of selected materials on which to obtain more quantitative results. In particular, it was important to know the optimum concentration of detecting agent in each matrix, the shortest time of exposure of the matrix to the contaminant gas resulting in a detectable reaction, and the lower limit of contaminant concentration in air to which the detector would react visibly. To achieve these aims, a volumetric system was assembled that would mix air accurately with a sample of test gas at concentrations as low as six parts per million. This set up is described in Appendix III.

The detecting materials tested in this phase of the investigation were the five detectors selected as the result of the screening work reported above, except that matrix A (60:40 cholesteryl nonanoate plus cholesteryl oleyl carbonate) replaced matrix B (40:40:20 cholesteryl phenyl carbonate plus cholesteryl nonanoate plus cholesteryl benzoate) in the cases where a detecting agent was added to the cholest base. This was done to increase the temperature sensitivity.

Other materials tested were matrices consisting of, again, matrix A by itself, to which were added separately triolein, methyl linolenate, methyl oleate, methyl linolenate and methyl linoleate combined, and castor oil. In addition, cholesteryl phenylhydrazine was tested alone.

The matrices containing cinnamyl alcohol and cinnamaldehyde had previously been shown to be very reactive to nitrogen dioxide attack when the latter was allowed to occur a few minutes after the preparation of the liquid crystal test samples. However, because of their relatively high vapor pressure the useful life of these detectors was relatively short.

Consequently, even though Figure 4.1 shows that the effect of nitrogen dioxide on a freshly prepared matrix containing cinnamyl alcohol lasts at least three days, the high vapor pressure of the compound and its companion, cinnamaldehyde, would seem to preclude their use as effective detectors.

Other materials which were tested at various contaminant concentrations and found inoperative were the combinations of matrix A with triolein and with castor oil. Cholesteryl phenylhydrazine also proved to be unreactive, at least under the conditions employed here.

Thus, in this continuing process of screening and checking likely candidates for the detection of nitrogen dioxide, attention was focused on the following four materials:

(a) Matrix A

Freshly prepared Matrix A was cast over test hoops and tested in the "Temperature vs Wavelength Apparatus" before and after exposure to 1000 ppm of nitrogen dioxide. Figure 4.3 shows the rather drastic

drop in color shift temperature caused by this contamination. It should be noted here that in comparing temperature (T) vs wavelength (λ) curves, one should bear in mind that the really useful portion of these curves is the one falling in the visible region, that is, approximately in the range between 4500 and 6500 Å, where most of the curves approach a linear form. For example, blue color appears at 4471 Å, the green color at 5015 Å, the yellow color at 5875 Å and the red color at 6560 Å. For visible comparison, then, one should check the "before" and "after" curves and determine at what temperature a certain color appears in both cases. In the case of curve 1 in Figure 4.3, the yellow color was visible at 39.4°C; in curve 2 this temperature corresponds to the ultra violet region.

Although Matrix A does show certain possibilities as a detector, subsequent work indicated that it is not as efficient at low contaminant concentrations as other detectors described later.

(b) Methyl Linoleate Plus Matrix A

Matrix A, plus 4% by weight of methyl linoleate, was exposed for 15 minutes to a contaminant concentration of 6 ppm. Figure 4.4 gives the results. This exposure indicates a small but positive reaction which appeared to last at least one day. The relatively small temperature difference between curves 1 and 2 indicates that the sensitivity range of this may be too narrow for easy detection.

(c) Methyl Linolenate Plus Matrix A

Figure 4.5 shows the effect of the contamination by 6 ppm of nitrogen dioxide on Matrix A plus 4% methyl linolenate as a function of exposure time. This material is much more sensitive to the attack of nitrogen dioxide traces than methyl linoleate. In fact even when the exposure time is reduced from 15 minutes to 10 minutes, the color shift temperature difference between uncontaminated and contaminated samples is larger than that occurring in the case of methyl linoleate at 15 minutes' exposure. Here then we find that the presence of three double bonds in the addendum definitely improves the reactivity of the liquid crystal detector.

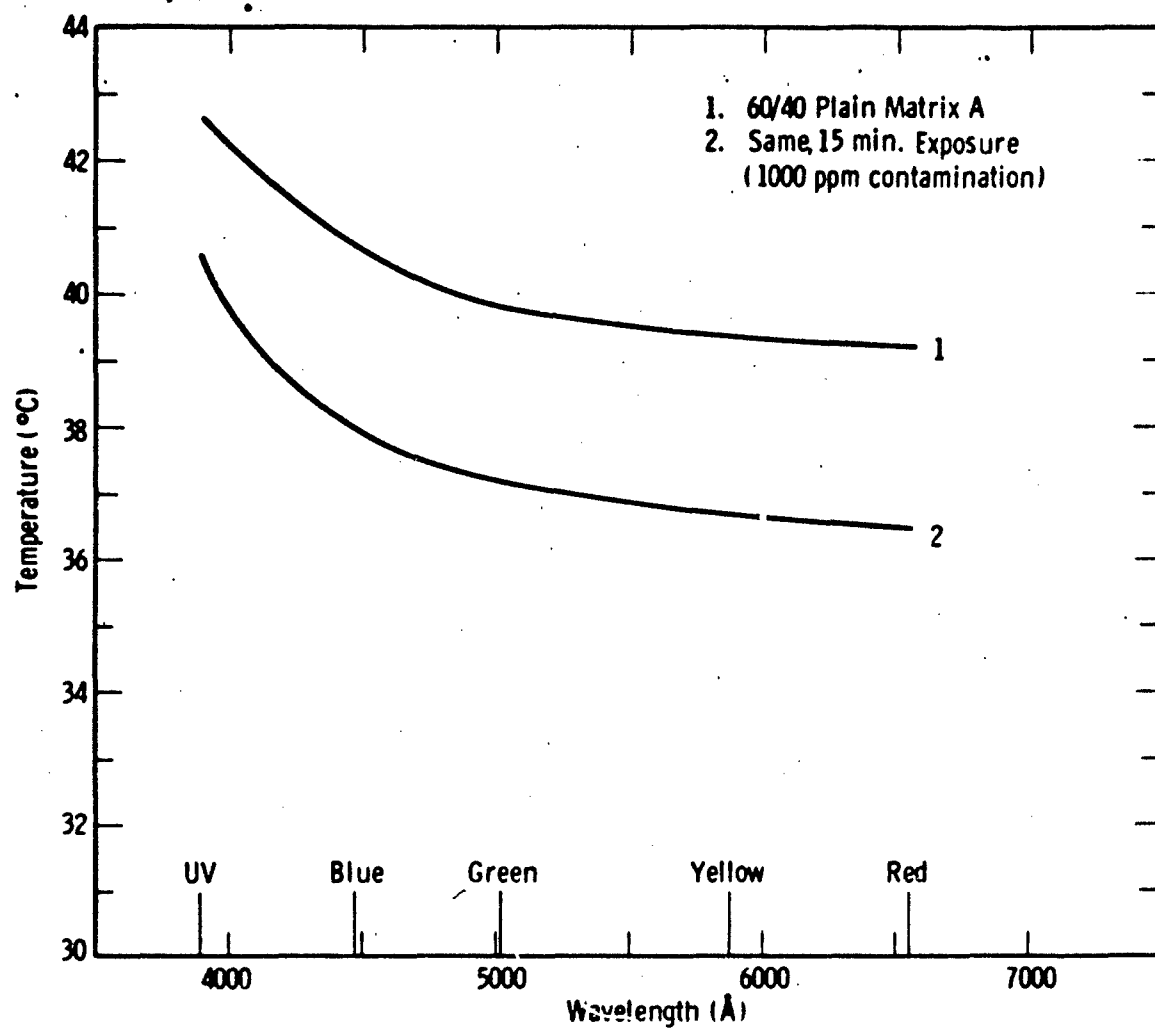


Figure 4.3 - Effect of 15 minutes exposure of Matrix A to 1000 ppm of NO_2 .

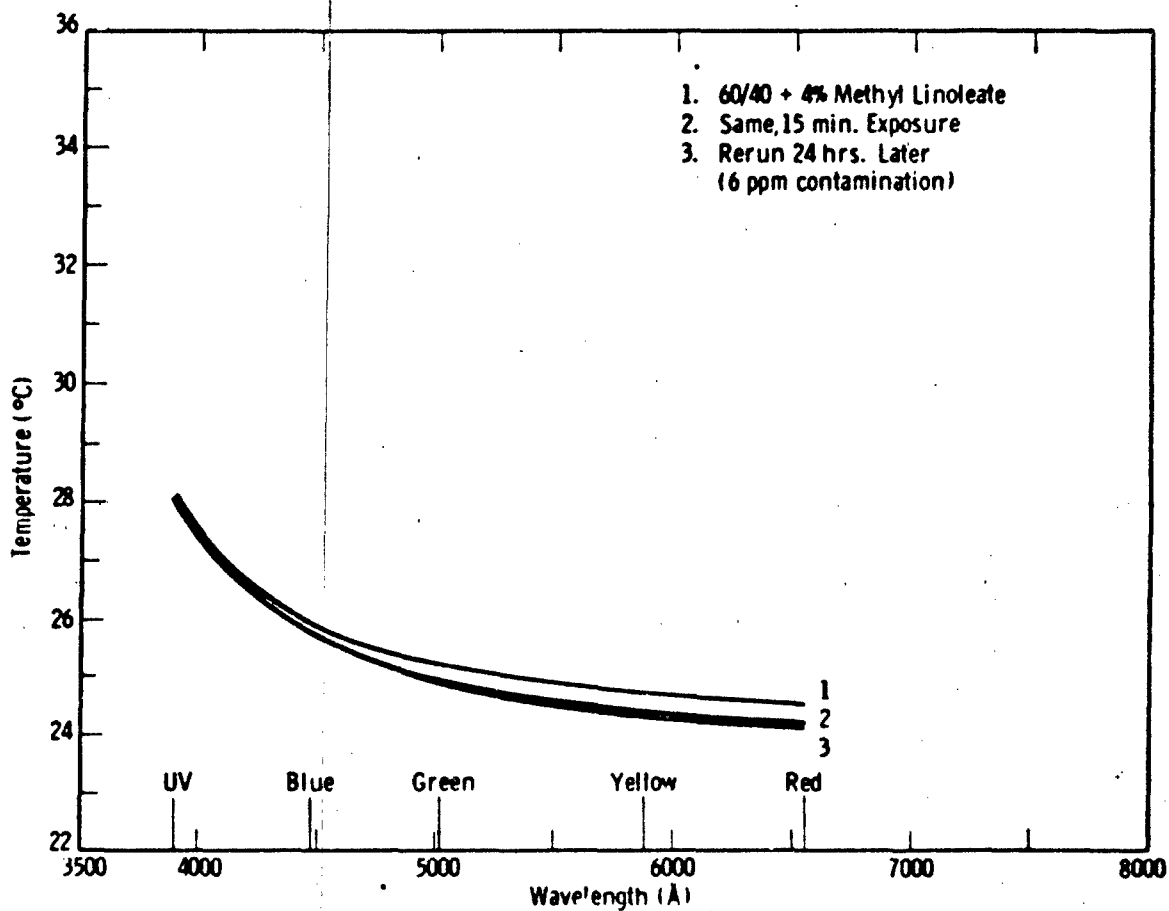


Figure 4.4 - Effect of 15 minutes exposure of Matrix A to 6 ppm of nitrogen dioxide + methyl linoleate and effect of 24 hrs. aging on exposed sample.

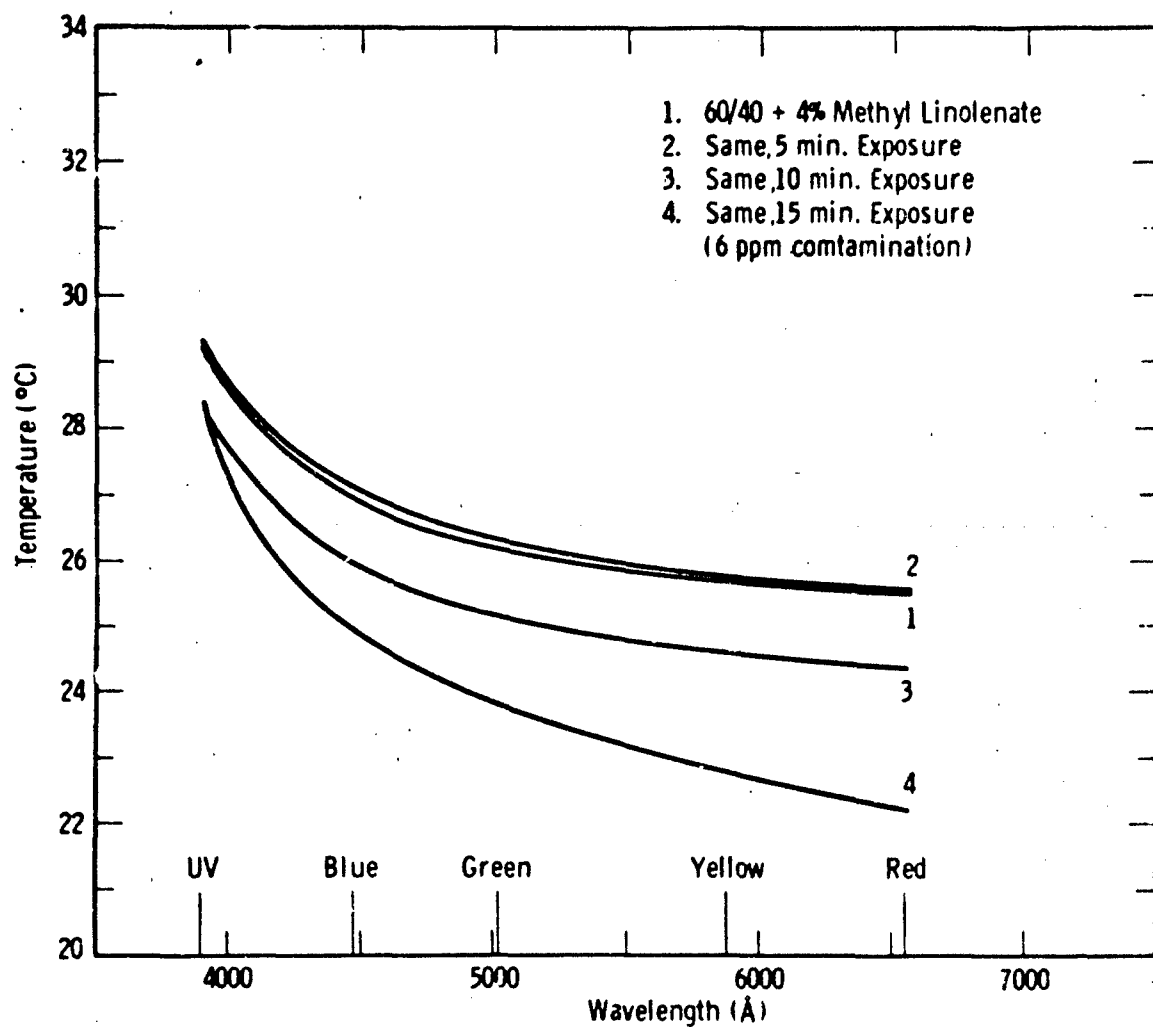


Figure 4.5 - Effect of exposure of 6 ppm of nitrogen dioxide on Matrix A + methyl linolenate for different exposure times.

(d) Oleic Acid Plus Matrix A

Figures 4.6, 4.7, 4.8, and 4.9 were introduced to show the type of experiments carried out to determine both the optimum concentration of the added detector (addendum) and the effect of decreasing contaminant concentration of each material at constant exposure time. These figures show that the amount of color shift between unexposed and exposed samples decreases as the NO_2 concentration decreases. Figure 4.6 also shows that the detector reactivity decreases as the addendum concentration increases, at a contamination level of 1000 ppm. At a contamination level of 100 ppm (Figure 4.7) the detector sensitivity remains approximately the same no matter what the addendum concentration. At a contamination level of 10 ppm (Figure 4.8), the reactivity seems to be inversely proportional to the addendum concentration. With a contamination level of 6 ppm (Figure 4.9), the results with 1% oleic acid plus Matrix A are unexpected and perhaps atypical; however, again the highest addendum concentration results in the lowest reactivity. It will be noticed also that in all cases the greater the detecting addendum concentration, the "cooler" is the detecting materials. An addendum (oleic acid) concentration of 3% by weight was then chosen to investigate the minimum exposure time necessary to obtain a visible reaction. Figure 4.10 shows the effect of different exposure times of 6 ppm of nitrogen dioxide on a matrix consisting of 3% oleic acid in Matrix A. With this material, an exposure of 15 minutes to 6 ppm of nitrogen dioxide seems to be necessary to obtain a visible reaction.

4.4 CONCLUSIONS

The aim of this phase of the reactive materials investigation was that of finding liquid crystal-type materials which could reliably detect very small quantities of nitrogen oxides, of the order of 1-10 ppm. As explained in Sec. 4.1, all the work was done with nitrogen dioxide, since no success was had in finding reactions with N_2O that

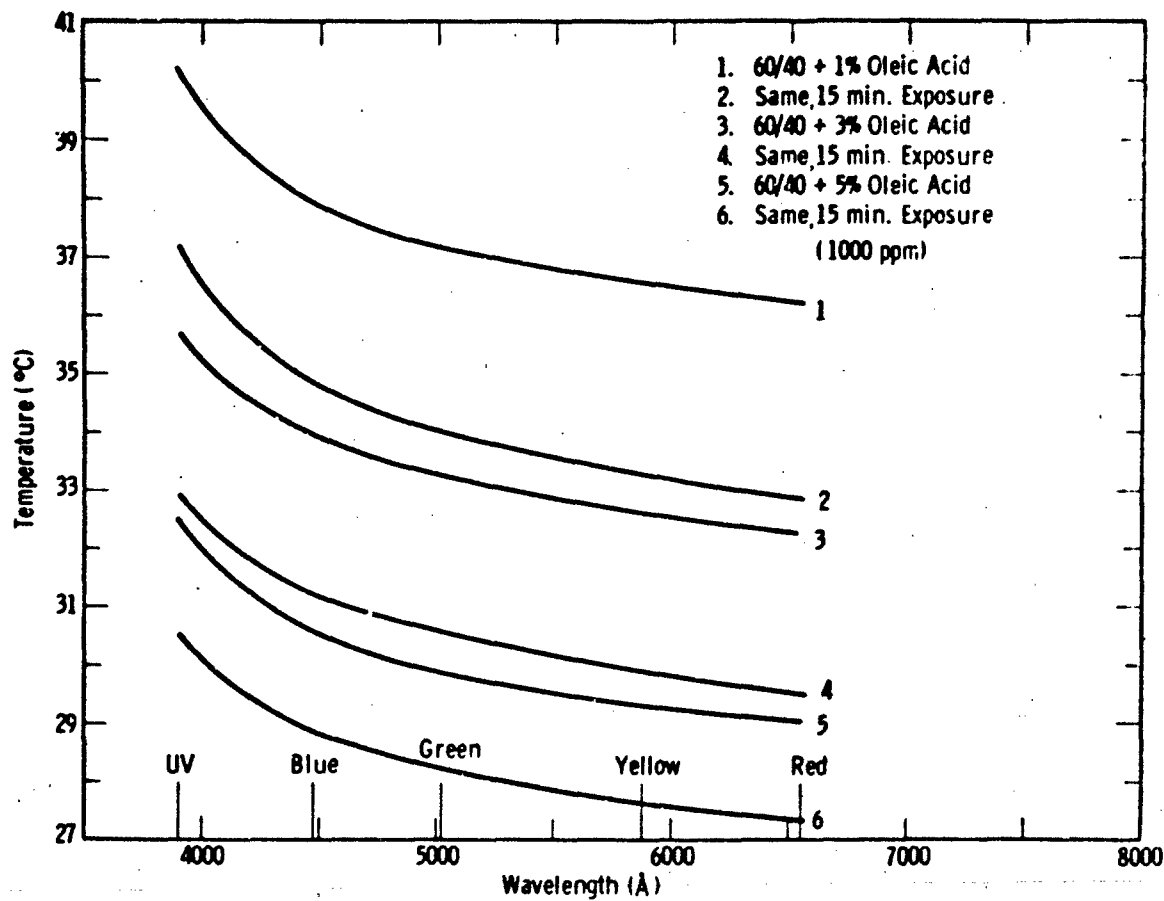


Figure 4.6 - Effect of 15 minutes exposure of 1000 ppm of nitrogen dioxide on Matrix A plus different concentrations of oleic acid.

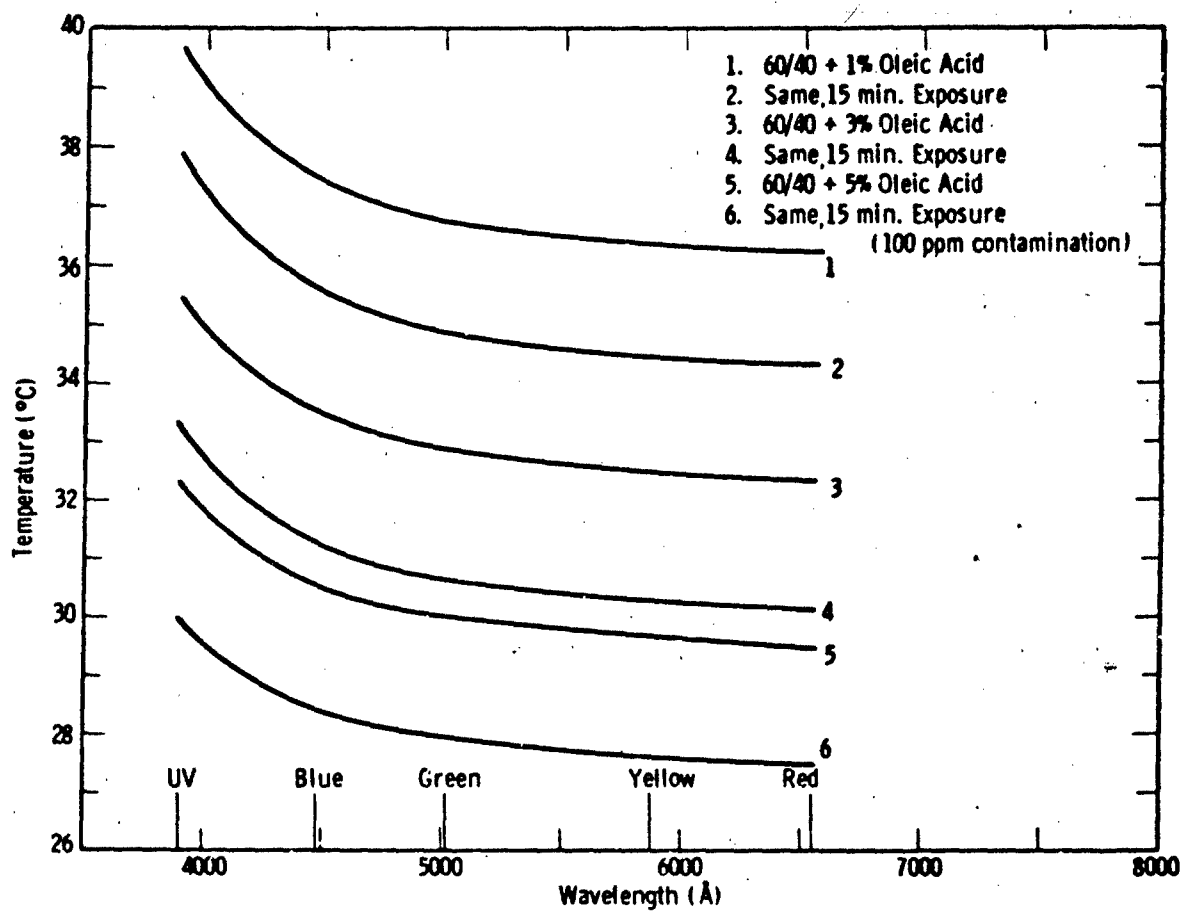


Figure 4.7 - Effect of 15 minutes exposure of 100 ppm of nitrogen oxide on Matrix A plus different concentrations of oleic acid.

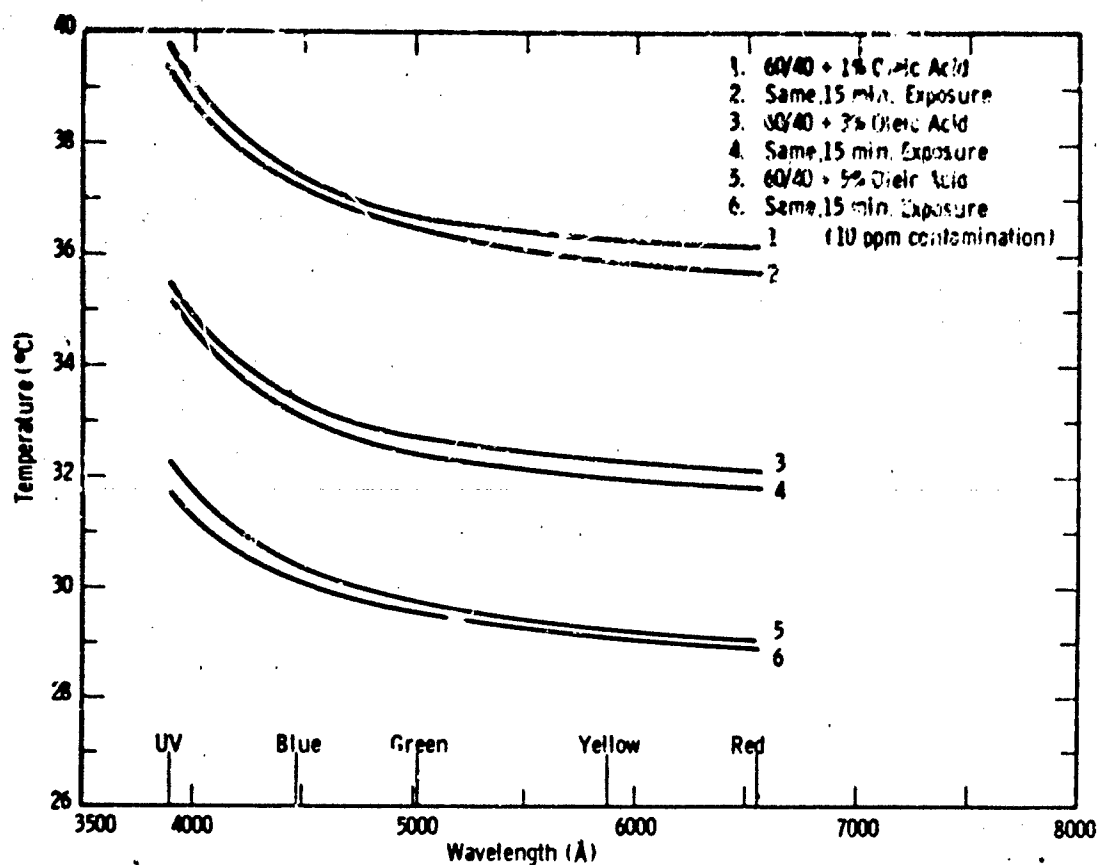


Figure 4.8 - Effect of 15 minutes contamination by 10 ppm of nitrogen dioxide on Matrix A added with different concentrations of oleic acid.

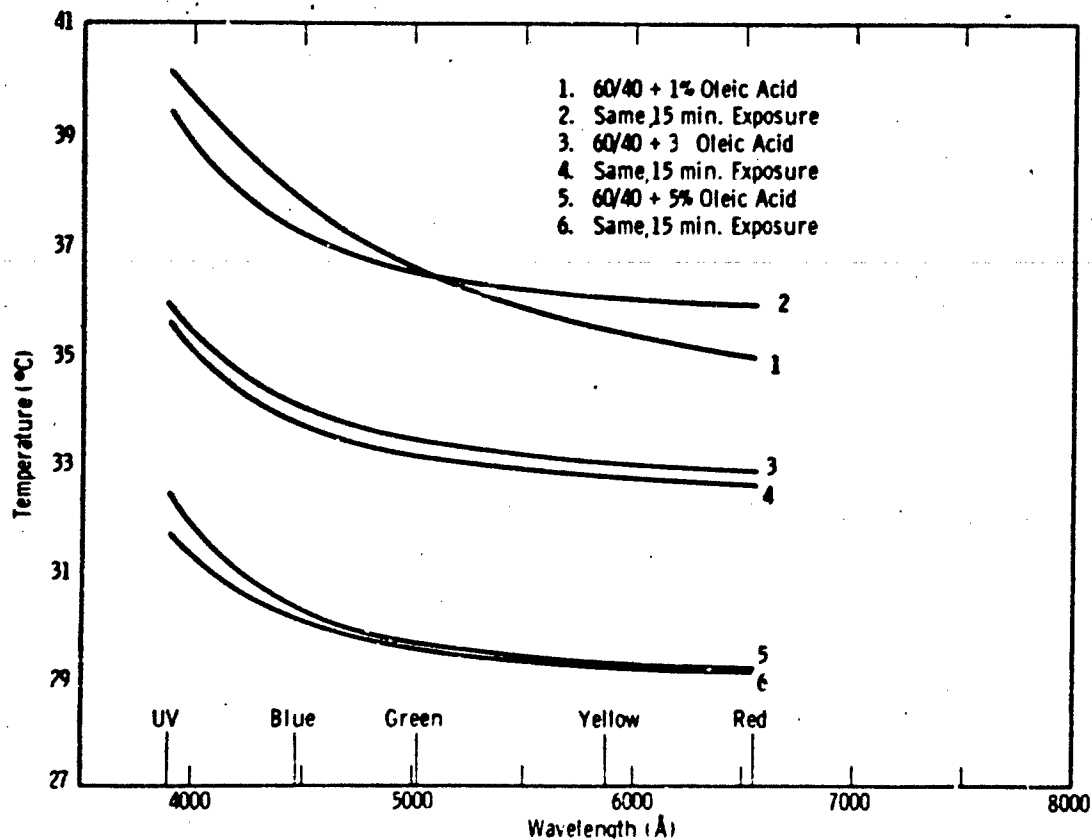


Figure 4.9 - Effect of 15 minutes exposure of 6 ppm of nitrogen dioxide on Matrix A plus different concentrations of oleic acid.

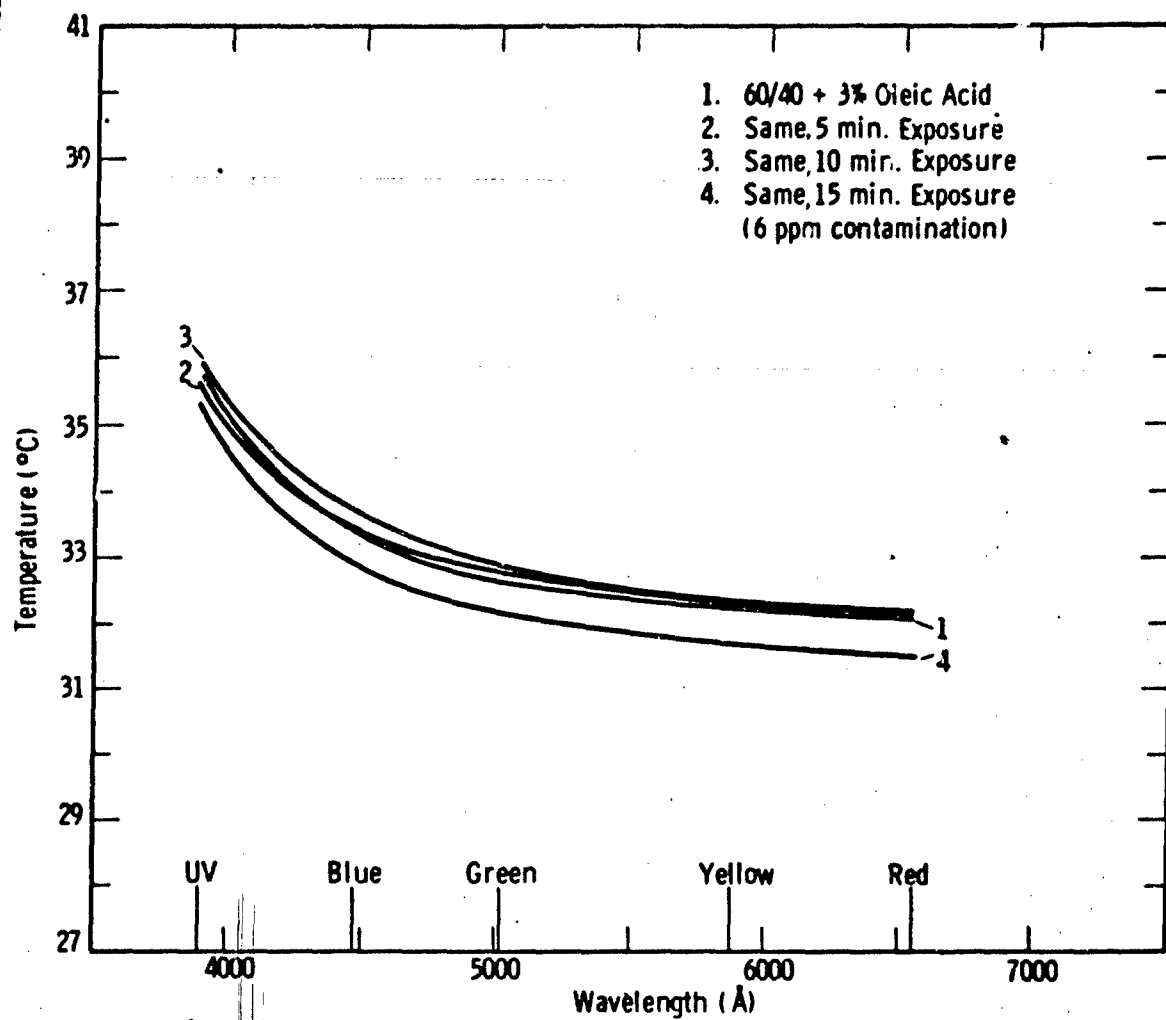


Figure 4.10 - Effect of exposure time of Matrix A with 3% concentration of oleic acid exposed to 6 ppm of nitrogen dioxide.

fell into the temperature range and conditions desired, and since the other oxides of nitrogen quickly revert to nitrogen dioxide when exposed to the atmosphere. Of the several materials investigated, and of the resulting likely candidates, two emerge as being relatively reliable and selective: Matrix A (60:40 cholesteryl nonanoate plus cholesteryl oleyl carbonate) + 3% oleic acid and Matrix A + 4% methyl linolenate. Exposure times of a minimum of 15 minutes for the former and of 10 minutes for the latter are suggested; sensitivity to 6 ppm of gas contaminant was demonstrated for both. Matrix A by itself might also be a good detector, and this possibility ought to be investigated. The two final detectors above and especially the one involving methyl linolenate, which is the more sensitive of the two by a small margin, provide detecting systems which are easily separated by attainable temperatures and which are activated reasonably quickly.

One must, however, bear in mind that the detecting system containing methyl linolenate was not tested for sensitivity to HCl, HF and UDMH, so that this system may not be selective. On the other hand, previous work with the very similar methyl linoleate did show selectivity for nitrogen dioxide, and therefore the methyl linolenate system might well be selective also.

4.5 REFERENCES

1. N.A. Khan, J. Chem. Phys. 23, 2447-8 (1955).
2. The Matheson Company, Inc., Nitrous Oxide Data Sheet.
3. Riebsomer, J.L., Chem. Rev. 36, 157 (1945).
4. Lapworth, A., and Mattram, E.N., J. Chem. Soc. 127, 1628 (1925).
5. Hilditch, T.P., J. Chem. Soc. 1828 (1926).
6. Porter, C.R., and Wood, B., J. Inst. of Petroleum, 37, 388 (1951).
7. Vasil'ev, S.V. Zhurnal Obshchei Khimii, 26, 712 (1956).
8. Vasil'ev S.V., Trudy Moskovskogo Instituta Tonkoi, Khimicheskoi Tekhnologii, M.V., Lomonosova, N. 5, p. 50 (1955).
9. Fuse, K. and Tamamushi, B., J. Chem. Soc. Japan 64, 338 (1942).
10. Schmidt, J., Ber. 33, 3241 (1920).
11. Stanford Research Institute, The Smog Problem in Los Angeles County, Jan. 1964, p. 53-61.

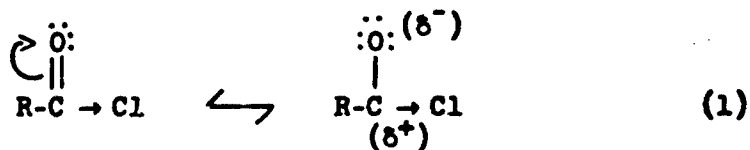
5. DETECTION OF TRACE HYDRAZINE AND UDMH

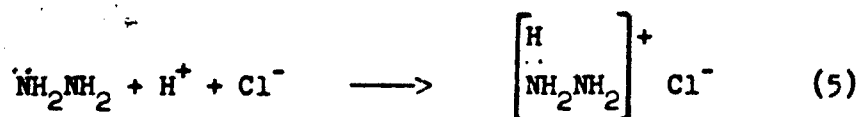
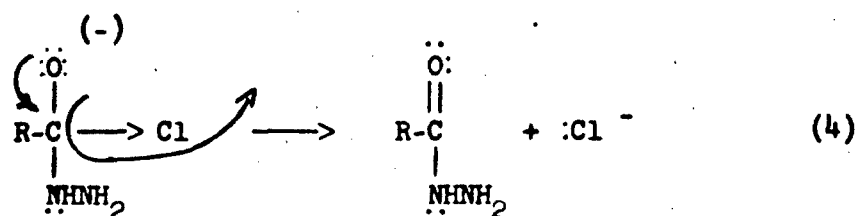
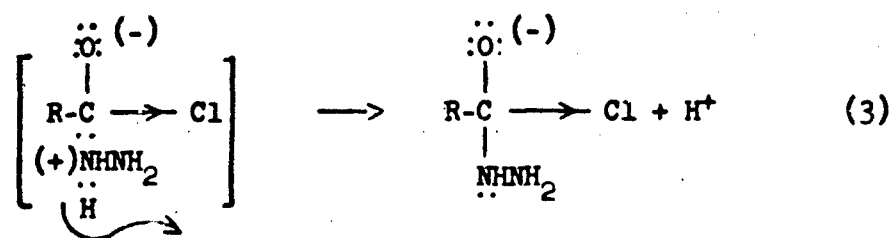
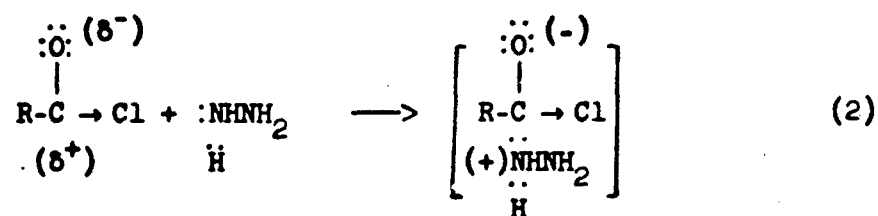
5.1 INTRODUCTION AND THEORY

For the detection and identification of hydrazine and its methyl derivatives six different reaction systems were investigated. These systems involved the reaction of hydrazines with

- a) chloroformates R-O-C(=O)-Cl
- b) acyl or aryl chlorides R-C(=O)-Cl
- c) the materials of (a) or (b) in conjunction with a proton acceptor (e.g., pyridine)
- d) the materials of (a) or (b) in conjunction with an alcohol (R-OH) with the hydrazine functioning as a proton acceptor
- e) β -diketones or β -ketoesters to produce pyrazole-type ring structures depending upon the degree of substitution of the hydrazine
- f) reactive allylic-type halogen compounds alone or in conjunction with an alcohol.

In systems a) and b) the over-all reactions are similar and can be formulated as follows (using hydrazine as the example). These reactions are nucleophilic in nature

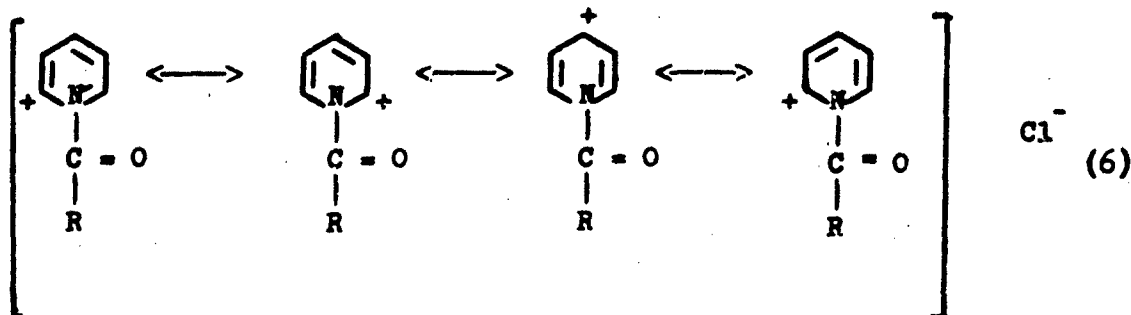




and may be considered to be initiated by the attack of a pair of electrons (on the nitrogen atoms) upon the carbon atom of the activated carbonyl group. Thus, step (1) is the normal activation of a carbonyl group arising from the greater electronegativity of the carbonyl oxygen atom as compared to the carbonyl carbon atom. The partial positive charge (δ^+) on the carbon atom becomes somewhat enhanced due to the inductive effect (electron withdrawal) of the chlorine atom. In step (2) the nucleophilic nitrogen atom attacks the positive center of the activated acyl halide molecule to produce the so called "transition state." This "transition state" may stabilize itself by the two step process illustrated in (3) and (4). The order of steps is probably as

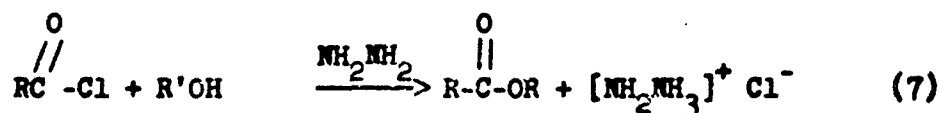
shown since the driving force can be thought of as the abstraction of the proton (H^+) by a second molecule of the nucleophilic hydrazine molecule (5).

The third reaction system, (c), investigated is similar to the series of reactions formulated for (a) and (b). The difference is the presence of a proton acceptor, other than hydrazine or its methyl derivatives, which is used as an additive to the liquid crystal matrix. By the use of an acceptor such as pyridine there is obtained a more reactive system, more reactive than systems (a) and (b) since the detecting media exists in the matrix in a reactive state. This reactive state is a transition-type state which can be stabilized by resonance (6):



Such systems have often been used for introducing acyl groups into other molecules. Systems such as these should be very sensitive to water or moisture in the atmosphere, more so than systems (a) or (b).

The fourth reaction system studied, (d), involved the reaction of chloroformates (or acyl or aryl halides) with an alcohol when catalyzed by the presence of hydrazine or its methyl derivatives acting as an activator and proton acceptor. The overall reactions may be written as:



The esterification reaction shown in (7) is a very useful tool in synthetic organic chemistry. Usually, however, a tertiary amine (e.g., pyridine) is used as the activator instead of primary or secondary

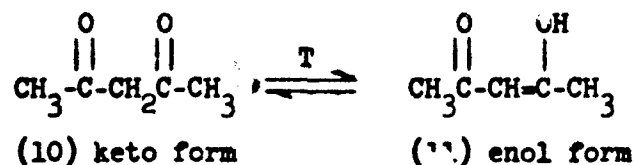
amines. This is obvious since primary and secondary amines can react with acyl halides to form amides (1-5) which will contaminate the desired esterified product.

The fifth reaction studied involved the interaction of hydrazines with either β -diketones (8) or β -ketoesters (9):



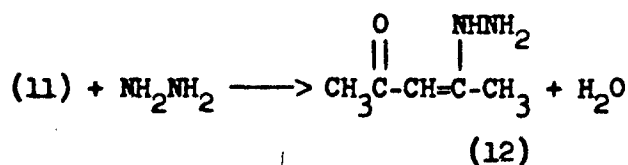
This method had the advantage that it should be able to differentiate between hydrazine, symmetrically substituted hydrazines, and unsymmetrically substituted hydrazines.

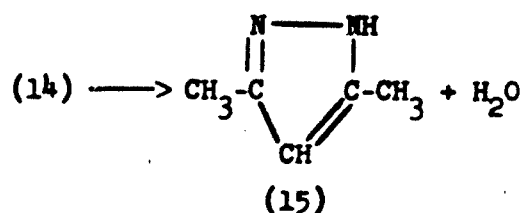
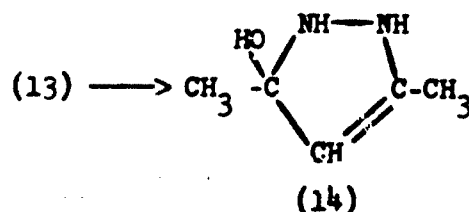
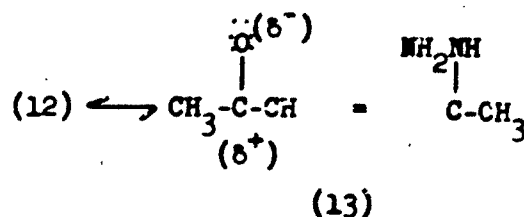
Both the β -diketone and the β -ketoester are capable of undergoing tautomerism and two forms can be written for each, a keto form and an enol form. Consider a β -diketone such as acetylacetone (10)



The enol form is capable of reacting with hydrazine, mono-substituted hydrazines, and symmetrically di-substituted hydrazines to form pyrazole derivatives. However, unsymmetrically di-substituted hydrazines are incapable of reacting to form these pyrazole-type ring structures.

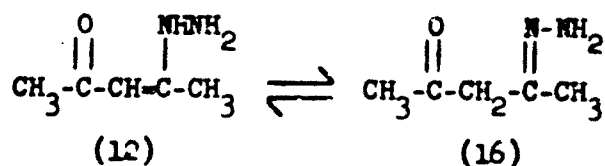
In the case of hydrazine and acetylacetone, the reaction may be visualized as follows. After establishing a tautomeric equilibrium, the hydrazine molecule reacts with the enol form (11) with the elimination of one molecule of water:

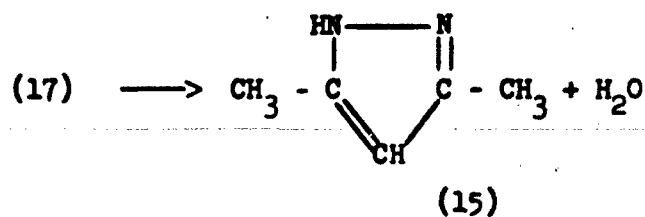
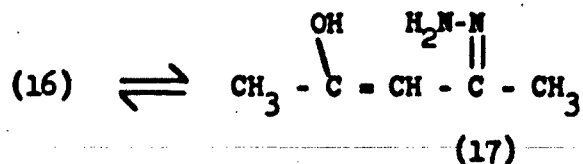




This molecule (12) can undergo carbonyl activation with (13) as the result. As shown earlier, the nucleophilic nitrogen atom can then attack the positive center of the carbonyl group (carbon atom) and by the transfer of a proton from the nitrogen atom to the negative center of the carbonyl group (oxygen atom) a neutral cyclic molecule (14) is formed. By the elimination of the elements of water from the nitrogen atom (the proton) and the adjacent carbon atom (the hydroxide ion) the compound 3,5 - dimethylpyrazole (15) is formed.

Another possible reaction mechanism leading to the same pyrazole derivative involves the formation of product (12) and then a tautomerism to (16).

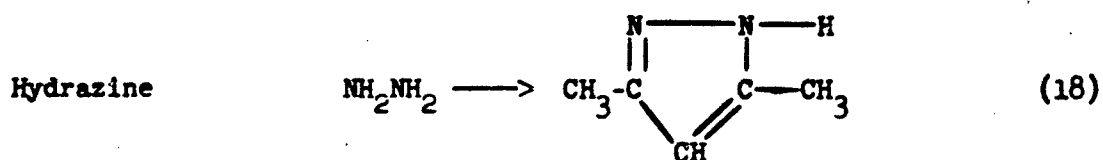




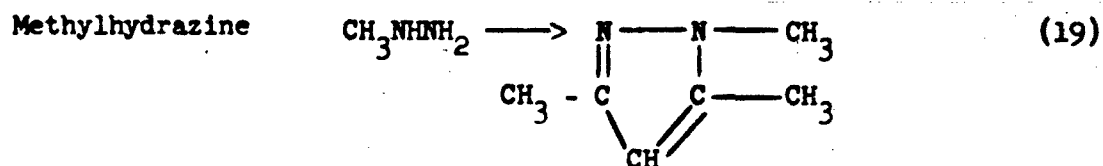
3,5 - dimethylpyrazole

Product (16) can exhibit enolization of the other carbonyl group to form (17) which can then lose the elements of water to cyclize and produce the 3,5-dimethylpyrazole (15).

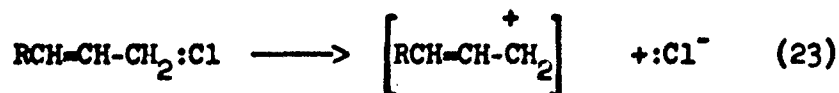
To illustrate the end products that could result if hydrazine and its methyl derivatives were to react with acetylacetone in this fashion, consider the following structures:



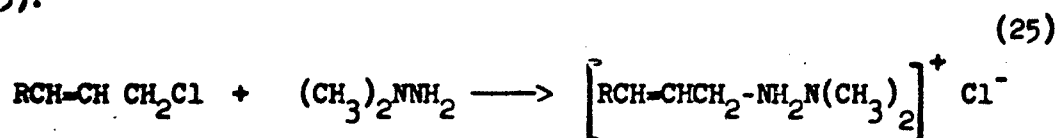
3,5 - dimethylpyrazole



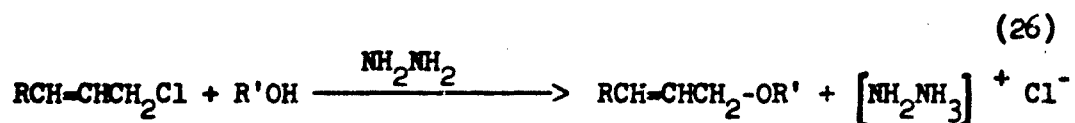
1,3,5 - trimethylpyrazole



The carbonium ion formed is a strong electrophile and should be capable of scavenging for electron dense materials, e.g., nitrogen compounds having available electrons. Since UDMH is a stronger base (see below) than hydrazine it could react with an allylic type halide as shown in (25):



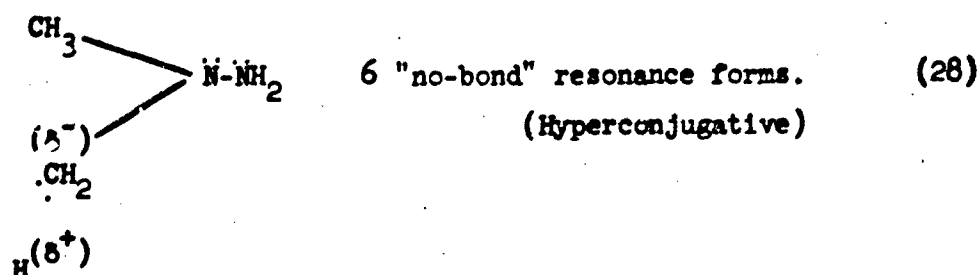
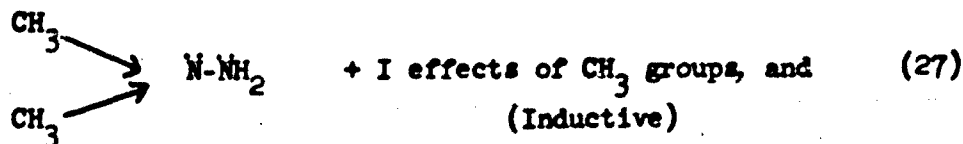
In the presence of alcohols, allyl halides may be induced to react by the presence of a proton acceptor, e.g., hydrazine (26):



Reactions as these were investigated as a possible means of differentiation as well as detecting the hydrazines.

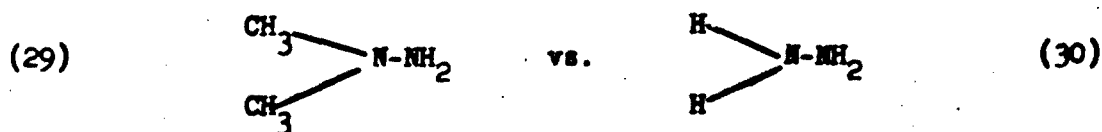
With hydrazine and unsymmetrical dimethylhydrazine it can be anticipated that there will be a difference in response to some of the preceding reactants. This difference can be attributed to the fact that the UDMH is more basic than hydrazine, and the UDMH will have a steric factor associated with it.

That UDMH is more basic than hydrazine results from both the inductive and the hyperconjugative effects of the two methyl groups. This may be illustrated as follows:



Both of these effects increase the basicity of the UDMH molecule by making the electron pairs on nitrogen more available for reaction.

The possible steric factor associated with UDMH (27) is caused by the spatial requirements of the two bulky methyl groups, as compared to two hydrogen atoms on hydrazine (28):



5.2 SCREENING TESTS

The same methods of liquid crystal film preparation with the incorporated detector(s) and sample delivery were used for the detection of hydrazine and unsymmetrical dimethylhydrazine (UDMH) vapors as was described earlier in Section 3.

For screening, the materials investigated as detectors were treated not only with the vapors of the materials to be detected but also with other nitrogen bases. As a representative group, the other vapors tested were ammonia, triethylamine, and pyridine. Table 5.1 shows the materials screened as detectors and the responses caused by

Table 5.1 - Materials Screened for UDMH, Hydrazine Detection.

Material	Structure	NH ₃	(CH ₃) ₂	Pyridine	UDMH	Hydrazine Hydrate
Dodecenyl chloride	$\text{CH}_3-(\text{CH}_2)_8-\text{CH}=\text{CH}-\text{CH}_2-\text{Cl}$	E	E	E	E	E
Dodecenyl chloride + oleyl alcohol	$\text{CH}_3-(\text{CH}_2)_8-\text{CH}=\text{CH}-\text{CH}_2-\text{Cl}$ + $\text{HO}-\text{CH}_2-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{CH}_3$	E	E	E	E	E
Oleyl chloroformate	$\text{CH}_3-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_8-\text{C}(=\text{O})-\text{Cl}$	E	A	A	A	A
Cholesteryl chloroformate + Pyridine	$\text{C}_{27}\text{H}_{45}\text{OCCl} + \text{Pyridine}$	E	A	B	B	B
Cholesteryl chloroformate	$\text{C}_{27}\text{H}_{45}-\text{C}(=\text{O})-\text{Cl}$	D	D	B	E	E
Cholesteryl chloroformate + cholesterol	$\text{C}_{27}\text{H}_{45}-\text{C}(=\text{O})-\text{Cl} + \text{C}_{27}\text{H}_{45}-\text{OH}$	F	F	F	F	F
Cholesteryl chloroformate + oleyl alcohol	$\text{C}_{27}\text{H}_{45}-\text{C}(=\text{O})-\text{Cl} + \text{C}_{18}\text{H}_{35}-\text{CH}$	C	C	C	C	C
Cholesteryl chloroformate + hexyl alcohol	$\text{C}_{27}\text{H}_{45}-\text{C}(=\text{O})-\text{Cl} + \text{CH}_3(\text{CH}_2)_4-\text{CH}_2-\text{OH}$	C	C	C	C	C
Oleyl terephthalyl chloride	$\text{CH}_3-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{CH}_2-\text{O}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{Cl}$	A	D	E	A	A
Cholesteryl terephthalyl chloride	$\text{C}_{27}\text{H}_{45}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{Cl}$	E	E	E	C	CB
Oleyl isophthalyl chloride	$\text{CH}_{18}\text{H}_{35}-\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{Cl}$	B	E	E	A	A
Cholesteryl isophthalyl chloride	$\text{C}_{27}\text{H}_{45}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{Cl}$	E	E	E	C	CB

Key

- | | |
|----------------------------------|--|
| A Strong increase in temperature | D Weak decrease in temperature |
| B Weak increase in temperature | E No reaction |
| C Strong decrease in temperature | F Color change (Temperature Insensitive) |

vapors of the five nitrogen-containing bases. All of the detector systems shown in the table represent the first four methods of detection described in the section above, i.e., chloroformates or acyl halides alone or in conjunction with an alcohol or pyridine, and (the sixth method of detection) allylic-type (reactive) halogen alone or with an alcohol. Of the methods and materials tested, it appeared that cholesteryl terephthalyl chloride, cholesteryl isophthalyl chloride, and cholesteryl chloroformate with an alcohol resulted in the greatest sensitivity.

The fifth method involved the use of β -diketones (or β -ketoesters). This method proved valueless when tested in the usual manner; i.e., vapors of hydrazine or UDMH did not cause a change in the liquid crystal film. Probably, for this reaction to succeed, a longer contact time between reactants is necessary.

5.3 SENSITIVITY TESTS

The method and apparatus used to test for and measure the response of UDMH were the same as described in Appendix III. As demonstrated earlier, this equipment allows for the delivery of gases or vapors of a known volume and known pressure so that by expansion into a larger known volume the concentration can then be determined.

In Table 5.2, the results are shown of exposing 8 ppm of UDMH for 15 minutes to 4% cholesteryl terephthalyl chloride. As can be seen, the operating temperature of the film was lowered more than 2 degrees in the visible region. At 44°C (see Figure 5.2) then, the eye would see that the wavelength of reflected light shifts from 6000 Å in the red region to 4200 Å in the blue region. The sensitivity is calculated to be $-0.29^{\circ}\text{C/ppm}$ of UDMH.

The mixture containing 4% cholesteryl isophthalyl chloride was found to be less sensitive (Table 5.3). After a 15 minute exposure to 8 ppm of UDMH this film exhibited a shift in the visible region of approximately -0.6°C (see Figure 5.1). Before exposure to UDMH, it would reflect light of a 6000 Å wavelength (red region), while after

exposure the reflected light would be at 5000 Å wavelength (green region). The sensitivity here was calculated to be $-0.075^{\circ}\text{C/ppm}$.

Temperature sensitive detectors were prepared by using mixtures of cholesteryl chloroformate (4%) in conjunction with cholesterol (molar amount based on the cholesteryl chloroformate) dissolved in a liquid crystal matrix of 60/40 cholesteryl nonanoate-cholesteryl oleyl carbonate. This material evidenced a response to UDMH as shown in Table 5.4. Comparison data of thick film vs thin film preparation showed the effects encountered when diffusion plays a part; i.e., the thin film evidenced a greater change than the thick film when treated in identical fashion.

Table 5.5 presents the data obtained using a detecting system of 4% cholesteryl chloroformate with an equimolar amount of oleyl alcohol in the usual 60/40 matrix. Exposure to 8 ppm for 15 minutes produced a negative shift of the color temperature.

The sensitivity tests for hydrazine-hydrate presented some problems that were not encountered in the UDMH tests. When hydrazine hydrate was placed in the volumetric dilution apparatus described in Appendix III, very little vapor pressure was noted. The vapor pressure of the hydrazine-hydrate at room temperature was found to be about 1 mm. The vapor pressure of hydrazine at 20°C is 10 mm while that of water at 20°C is 18 mm. Since considerable hydrogen bonding does take place in a liquid solution of hydrazine and water, as evidenced by several physical properties, the vapor pressure of hydrazine-hydrate might be expected to be less than that of either of the two individual liquids. Data are available⁽¹⁾ to substantiate that vapor pressures of hydrazine-water mixtures exhibit a negative deviation from Raoult's Law and that the vapor pressures of the individual constituents are smaller than might be calculated from the mole fraction of each. This low vapor pressure of hydrazine-hydrate made it impractical to achieve the desired 10 ppm with the volumetric dilution apparatus that was used for the UDMH. Therefore, the method used was the hypodermic syringe technique described in Section 3.2. The calculated vapor existing

Table 5.2 - Detection of UDMH with 4% Cholesteryl Terephthalyl Chloride in 60/40 Cholesteryl Nonanoate - Cholesteryl Oleyl Carbonate.

<u>Color Reflected</u>	<u>Wave-length (A)</u>	<u>Temperature</u>		
		<u>Unexposed</u>	<u>15 min. Exposure 8.13 ppm</u>	<u>Temp. Change</u>
UV	3888	48.12°C	45.91°C	-2.21°C
Blue	4685	-	-	-
Green	5015	-	-	-
Yellow	5875	44.07-44.19	41.76	-2.31 to -2.43
Red	6560	-	-	-

Table 5.3 - Detection of UDMH with 4% Cholesteryl Isophthalyl Chloride in 60/40 Cholesteryl Nonanoate-Cholesteryl Oleyl Carbonate.

<u>Color Reflected</u>	<u>Wave-length (A)</u>	<u>Temperature</u>		
		<u>Unexposed</u>	<u>15 min. Exposure 8.13 ppm</u>	<u>Temp. Change</u>
UV	3888	41.93°C	41.29°C	-.64°C
Blue	4685	39.55	38.91	-.64
Green	5015	38.76	-	-
Yellow	5875	38.14	37.50	-.64
Red	6560	37.78	37.19	-.59

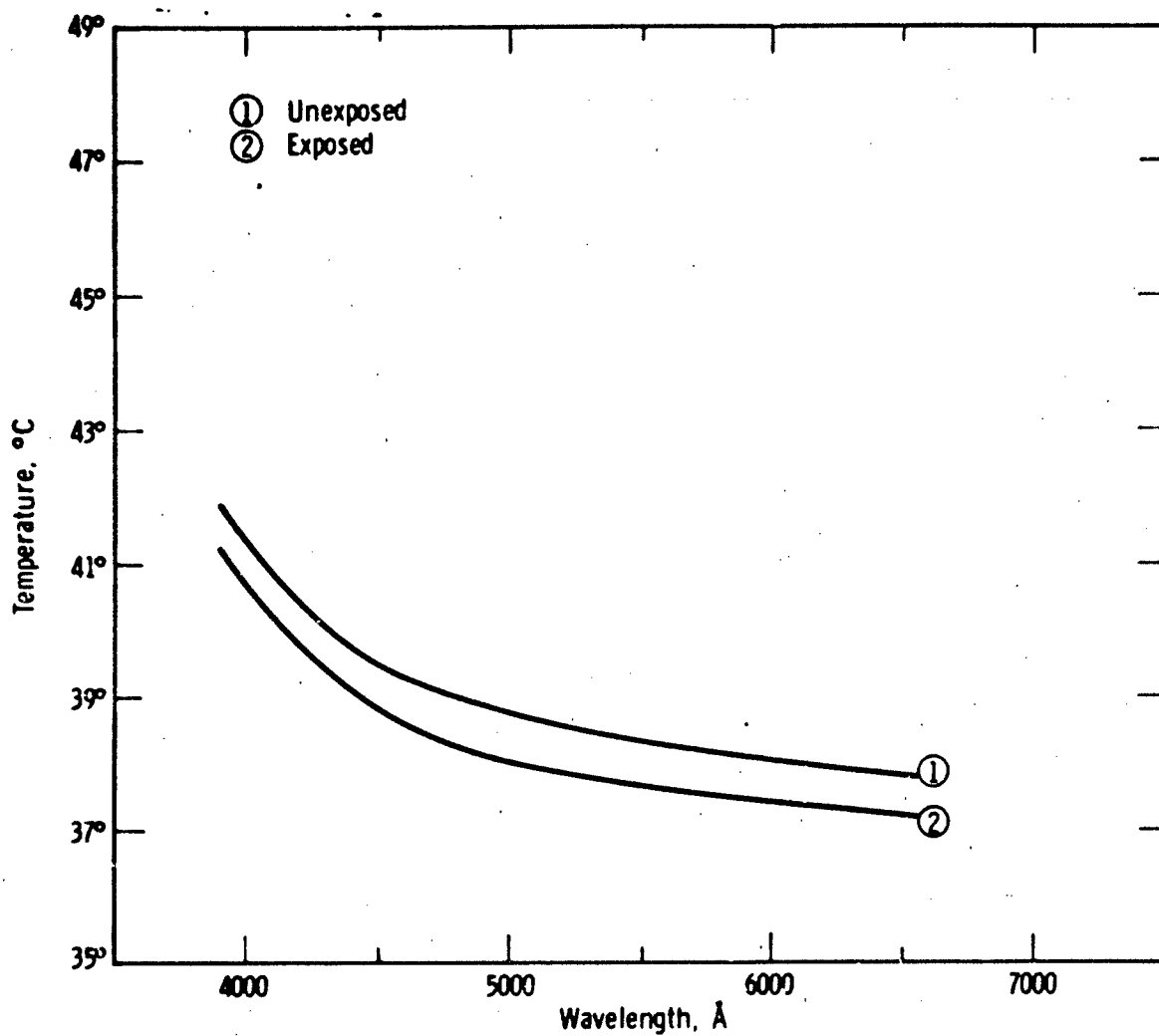


Figure 5.1 - Effect of 15 min contamination by 8 ppm UDMH on Matrix A + 4% Cholesteryl Isophthalyl Chloride.

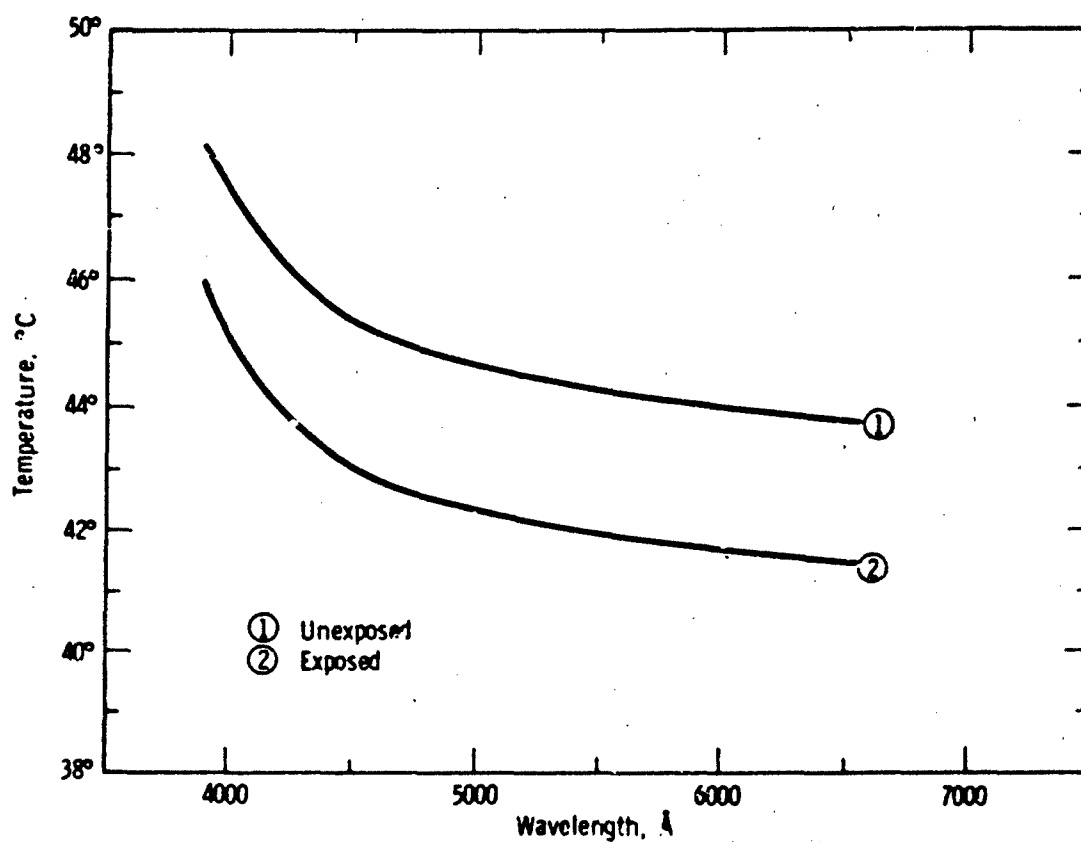


Figure 5.2 Effect of 15 min exposure by 8 ppm UDMH on Matrix A + 4% Cholesteryl Terephthalyl Chloride.

Table 5.4 -- Detection of UDMH with 4% Cholesteryl Chloroformate + Cholesterol in 60/40 Cholesteryl Nonanoate-Cholesteryl Oleyl Carbonate for Thick and Thin Films.

Color Re- flected	$\lambda(A)$	<u>Test of Thick Film</u>			<u>Test of Thin Film</u>		
		<u>Temperature</u>			<u>Temperature</u>		
		Unexposed	15 min 8 ppm	Temp. Change	Unexposed	15 min 8 ppm	Temp. Change
UV	3888	37.07 - 36.59	36.59 - 36.24	--	35.84°C	35.02°C	-.82°C
Blue	4685	30.90°C	30.92°C	+0.02°C	--	35.48	--
Green	5015	30.02	29.90	-.12	--	--	--
Yellow	5875	29.20	29.18	-.02	28.95	29.22	+0.27
Red	6560	28.64	28.59	+0.05	--	--	--

Table 5.5 - Detection of UDMH with 4% Cholesteryl Chloroformate + Oleyl Alcohol in 60/40 Cholesteryl Nonanoate-Cholesteryl Oleyl Carbonate.

Color Reflected	$\lambda(A)$	<u>Temperature</u>		
		Unexposed*	15 min 8 ppm	Temp. Change
UV	3888	23.05°C	20.38°C	-2.67°C
Blue	4685	18.00	17.58	-.42
Green	5015	16.82	16.42	-.40
Yellow	5875	15.70	15.68	-.02
Red	6560	15.07	15.12	+ .05

*After 1 day standing

above liquid hydrazine hydrate is 1000 ppm. Using the syringe this concentration was reduced to 100 ppm and then to 10 ppm. Using a detector of 4% by wt. cholesteryl chloroformate and cholesterol (equimolar) in a 60/40 matrix, hydrazine-hydrate did not give a satisfactory response. However, the 8% cholesteryl chloroformate and 8% cholesterol in a 60/40 matrix gave an identical response as that obtained with UDMH. Using this as a basis of comparison, the 4% cholesteryl terephthalyl chloride and 4% cholesteryl isophthalyl chloride containing liquid crystal systems were exposed to HH. The result was a depression of 1 to 2°C for the terephthalyl derivative and a depression of approximately 0.5°C for the isophthalyl derivative. Upon standing, this difference gradually diminished and ultimately became slightly positive, i.e., the operating temperature was raised. Further work is needed to determine the mechanism of this effect. The detection of UDMH indicated a change in the slope of the temperature vs wavelength curve rather than a shift in the operating temperature. This indicated that the reactions for this material could be readily adapted to temperature insensitive systems. Three systems were made which were temperature insensitive. The most sensitive used a catalytic mechanism. It contained, by weight:

- 30 parts cholesteryl oleyl carbonate,
- 20 parts cholesteryl nonanoate,
- 8 parts cholesterol, and
- 8 parts cholesteryl chloroformate.

This material shifted from a green color to a deep red at 8 ppm at 24°C. Before exposure the material was temperature insensitive; after exposure the material changed color with a change in temperature. This material could probably be improved by adding cholesteryl chloride. Because of a lack of time this procedure was not investigated. Simple amines were shown to interfere with the results of this test. However, if UDMH or hydrazine are known to be present, it could be used as a quantitative test.

The two remaining materials were made using mono-cholesteryl isophthalyl chloride and mono-cholesteryl terephthalyl chloride. These formulations (by weight) are as follows:

UDMH#1

- 2 parts cholesteryl terephthalyl chloride
- 7 parts cholesteryl oleate
- 1 part cholesteryl nonanoate
- 2 parts cholesteryl chloride

UDMH#2

- 2 parts cholesteryl isophthalyl chloride
- 7 parts cholesteryl erucyl carbonate
- 1 part cholesteryl nonanoate
- 2 parts cholesteryl chloride

Although these materials are of lower sensitivity than the preceding mixture, they give a test which is not interfered with by any of the gases or vapors used in this contract.

5.4 CONCLUSIONS

The qualitative detection and distinction between hydrazine (and its methyl derivatives) and a number of other basic molecules has been successful. The number of detection mechanisms available and the results obtained show the versatility of a test which is based on the cholesteric system when applied to moderately complex molecular structures. In the tests for sensitivity, the results were not as strong as with HCl or HF; however, concentrations of 1 to 10 ppm could be detected.

The unusual effect of hydrazine and UDMH with terephthalyl chloride derivatives should be further studied with an attempt to determine the mechanism involved. This reaction is potentially very useful in leading to reactive materials which have high sensitivities and the ability to distinguish minute differences in molecular structure.

Temperature insensitive materials were developed with this group of materials which show the validity of earlier work in this area. The interpretation of the temperature vs wavelength curves was used to imply that a nontemperature sensitive material could be made. This was experimentally verified.

5.5 REFERENCE

1. The Chemistry of Hydrazine, L. F. Audrieth, B. Ackerson, John Wiley and Sons, Inc., New York (1951) p. 105.

6. DETECTION OF TRACE HNO_3

As a side result of this work, cholesteryl phenyl hydrazine which was prepared as a possible detector of HCl and HF has been found to be reactive to HNO_3 at the 1 to 10 ppm level, but not to the oxides of nitrogen or to HCl or HF . This is an important result since the oxides of nitrogen will form HNO_3 in the presence of water vapor. Under some circumstances this should be a valuable aid in gas analysis. The material was prepared for testing by placing 10% by weight of the hydrazine in 55% cholesteryl oleyl carbonate and 35% by weight cholesteryl nonanoate. Using a hypodermic syringe and the technique described earlier, a shift in the color temperature in excess of 1°C occurred for a concentration estimated at 1 ppm or less.

By adding 4% cholesteryl phenyl hydrazine to a matrix that was composed of equal parts of cholesteryl nonanoate and oleyl cholesteryl carbonate a detector was prepared that reacts to HNO_3 but not to HF and HCl . The color transition temperature is raised more than 1°C upon exposure to 8 ppm concentrations of HNO_3 for 15 minutes.

Since work on this material was not required under the present contract, the effect was not studied at great length. Indications are that it might prove useful for a non-temperature sensitive material. However, this has not been experimentally proved. This would be accomplished by using a matrix containing cholesteryl chloride as a major constituent (see Appendix I).

7. CONCLUSIONS AND RECOMMENDATIONS

HCl and HF. Suitable materials for detecting HCl and HF at concentrations of 1 ppm were developed. With the temperature and pressure restrictions that were imposed it was not found practical to distinguish between HCl and HF. If some particular application demands a differentiation between them, future work is recommended.

HH and UDMH. Several temperature insensitive detectors were developed that reacted to both HH and UDMH at concentrations of the order of 10 ppm. Temperature sensitive materials were found that would distinguish between these two gases at concentrations of 8 ppm.

Oxides of Nitrogen and Nitric Acid. NO_2 gas was detected at a contamination level of 6 ppm with a number of cholesteric liquid crystal materials. In the presence of water vapor in the atmosphere, NO_2 will form HNO_3 . Since water vapor generally occurs in the atmosphere, a detector was devised to react to HNO_3 at a concentration level of 8 ppm.

Gas Mixtures. Some of the gases studied if mixed in the atmosphere would react with each other, e.g., hydrazine and HCl. However, mixtures of a number of these materials are possible. In principle, the detection of mixtures presents no problem if the liquid crystal reacts to only one group. For instance, the detection of NO_2 in the presence of HCl is not a problem. On the other hand, detection of small amounts of HCl in the presence of large amounts of NO_2 is not quite so simple. To decrease the reactivity of the HCl detectors to NO_2 , further investigation is required.

UDMH and HH will not interfere with any of the other reactive materials. NO_2 will in some cases react with the detector matrix, so the detection of UDMH & HH in the presence of NO_2 is a problem. However, the chance of finding UDMH or HH with NO_2 is extremely remote due to the formation of nitric acid in the presence of water vapor followed

by the rapid decomposition of the HH or UDMH. NO_2 can be detected and identified even when other gases are also present.

Quantitative Analysis. The feasibility of quantitative and qualitative tests has been demonstrated using cholesteric liquid crystals. It is recommended that experiments be carried out with these materials to establish a standard set of exposure techniques with controlled motion of the contaminant atmosphere across the detectors to obtain a set of quantitative calibrations. These calibrations should also be established as a function of temperature.

Life of Detectors. We believe that the life of these detectors, when kept away from reactive materials in the atmosphere and protected from sunlight, will be indefinite at any temperature up to the boiling point of the solvent. However, extensive life tests should be made. When these materials are exposed to the atmosphere, their life may be expected to be very limited due to traces of reactive gases. Hence care must be taken in storage.

Extension to Other Gases. From the results of this program, it appears that many other gases and vapors can be detected at low concentrations using this important new technique.

Appendix I

BACKGROUND INFORMATION ON LIQUID CRYSTALS

I.1 INTRODUCTION

The cholesteric phase represents a unique situation in nature. In this phase a highly colored material does not absorb incident radiation but transmits and scatters light selectively. The colors are not dependent upon specific electronic arrangements in the materials like more familiar dyes but, instead, are dependent on such things as steric factors, (molecular shape) and dipole arrangement. Thus materials which exhibit liquid crystal properties may be affected by a difference in carbon chain length or by the position occupied by a methyl group. The unique properties of this material allow it to be used in a new analytical technique. Such relations as Beer's law do not hold when two materials are mixed. The materials do not give two color peaks but only one which represents the net effect of the molecules in the system. As a result, this average effect allows us to arrive at color effects for reactions which involve non-colored reactive materials. The degree of the change in the optical properties of the liquid crystal represents the magnitude of these reactions.

Our general approach to the problems of developing a liquid crystal gas detector is to choose a class of compounds that will react with the gas and which can be incorporated into a suitable liquid crystal.

I.2 OPTICAL EFFECTS

The cholesteric phase was the first liquid crystalline state observed. The discovery was in part due to its unusual optical properties. Like most crystalline materials, it acts as a birefringent material. However, at that point the resemblance ends. The optical

properties may be summarized as follows: (1) The cholesteric structure is uniaxial and optically negative while other liquid crystal structures are optically positive; thus, for the cholesteric phase, there is a single optical axis normal to the surface along which the index of refraction has a minimum value. (2) The cholesteric structure is optically active with rotary powers many times that of common optically active materials. The plane of linearly polarized light is rotated through an angle several hundred times that of the usual optically active materials, such as sucrose or optically active quartz. (3) When illuminated with white light, the cholesteric structure scatters the light to give an iridescent color, which varies with substance, temperature, and angle of the incident beam. (4) The cholesteric structure is circularly dichroic for some wavelength region, that is, one circularly polarized component of the incident beam is transmitted without attenuation, whereas the other is scattered. Either the right or the left hand circular polarized component may be affected.

These optical properties depend on a delicately balanced molecular arrangement. A change of shape or dipole moment or any other disturbance which interferes with the weak forces between molecules results in a dramatic change. Reflection, transmission birefringence, circular dichroism, and optical rotation, all undergo marked transformations.

No complete theoretical treatment of the optical properties of the cholesteric state is available, but Oseen¹ and deVries² have considered these optical properties for normal incident light. The latter used as a model, a number of birefringent planes, each containing its own optical axis and each displaced a little from the plane immediately below it as shown in Figure I.1. The various optical axes represented by the arrows describe a helical structure with pitch equal to the wavelength of light scattered at normal incidence. Unfortunately, the usefulness of this model is severely limited, since it explains only the effects of normal incident light.

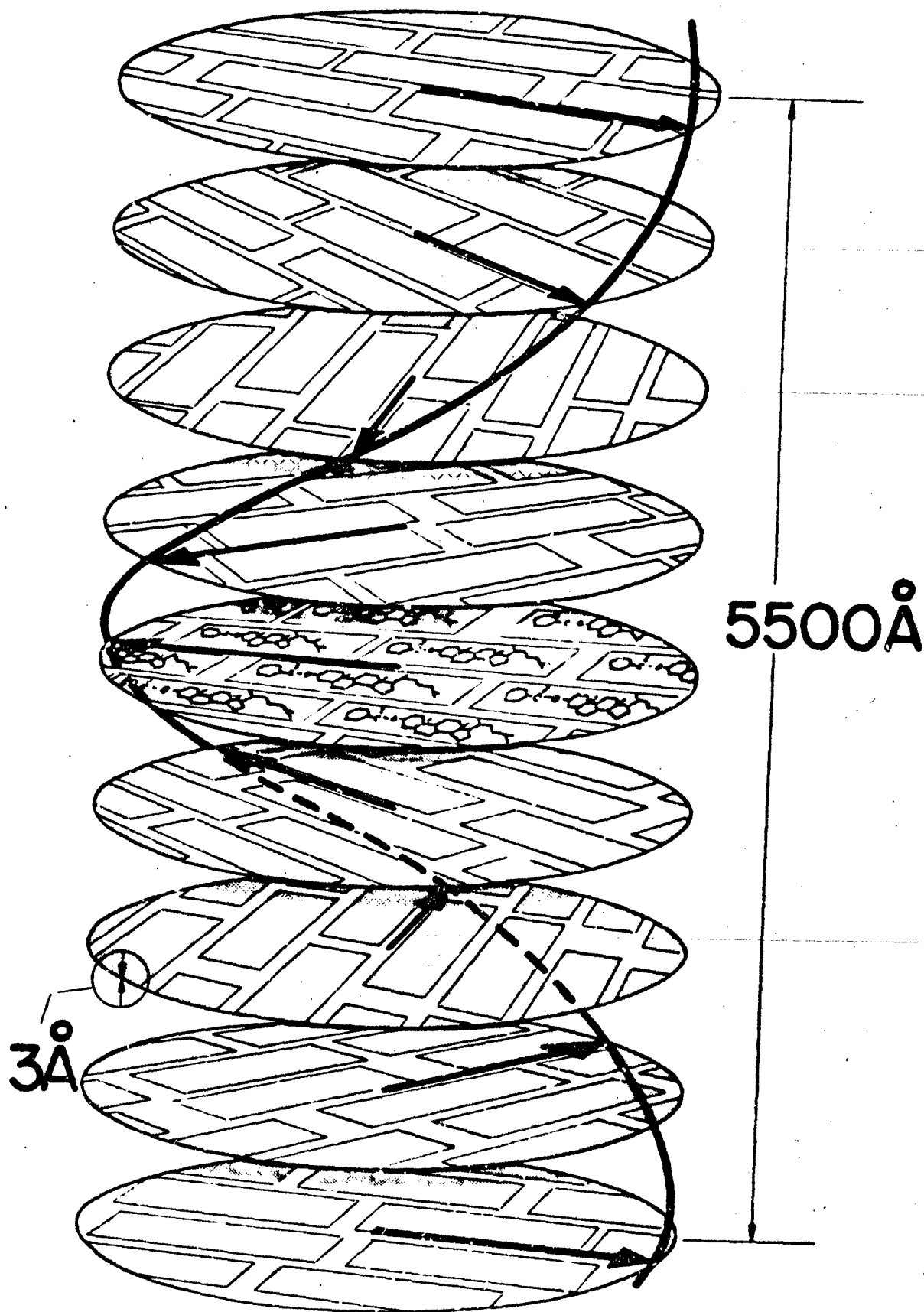


Figure I.1 - Schematic representation of helical model of the cholesteric phase.

1.3 MOLECULAR STRUCTURE

Early in the liquid crystal program it was discovered that gases, liquids and solids can affect the structure of the cholesteric liquid crystals so that one or more of the optical properties are permanently or temporarily changed. By utilizing this general principle, an entirely new mode of analysis has been developed. The program with RADC is concerned with chemical reactions which are not reversible. Changes occur in the optical properties of the liquid crystal upon exposure. These measured or observed optical effects are a function of the total exposure time as well as the concentration of the gas to be detected. In order to predict the effects of any one of the gases and how they will affect a specific cholesteric liquid crystal, a review of the effect of molecular structure is necessary.

The cholesteric liquid crystal state is primarily associated with the derivatives of sterols. Although cholesterol does not itself exhibit a liquid crystalline phase, an examination of the structure described by various investigators³ explains the formation of this phase. To understand the structure of cholesterol, the tetrahedral bond angles of carbon should be visualized. See Figure I.2.

If the methyl groups at C_{10} and C_{13} are visualized as projecting out of the plane of the paper, the side chain at C_{17} and the hydroxyl group at C_3 will also project above the plane of the paper while the hydrogen atoms which are shown with a dotted bond line project below the plane of the paper. The result is a molecule which has a broad flat configuration that may be visualized as zigzagging through the plane of the paper with one edge relatively smooth and one edge roughened by the side chain.

As one of the ways of determining the effect of molecular structure on the cholesteric phase, experiments were performed in which the general planar configuration of the molecule was altered. This was done by saturating the double bond at C_5 . If cholesterol is hydrogenated, the hydrogen at C_5 projects down and the general plane of the molecule is preserved. This compound is also found associated

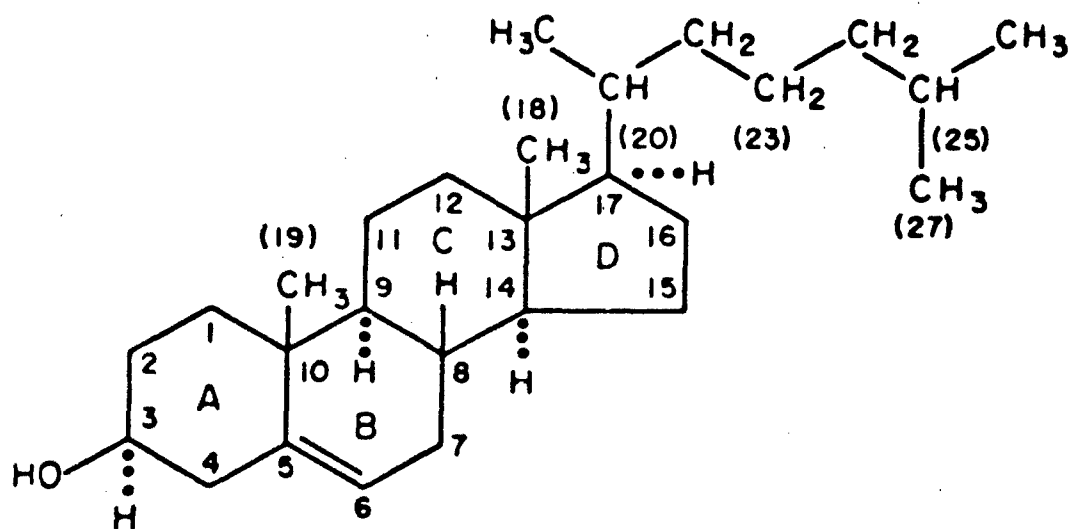


Figure I.2 - The structural formula of cholesterol.

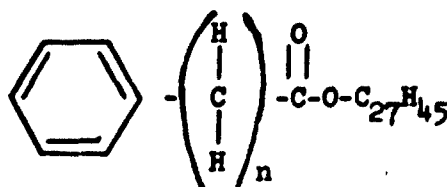
with cholesterol and is called cholestanol. The cholesterol-derived compound which has the hydrogen at C₅ projecting out of the plane is called coprostanol and is one of the elimination products of animals. In this case, the A ring is bent into the plane of the paper giving almost the effect of a hook. All of the cholestanol compounds studied have a cholesteric phase which is optically indistinguishable from the phase formed by cholesterol derivatives. These derivatives include cholestanyl benzoate, cholestanyl nonanoate, cholestanyl acetate, and cholestanyl dihydrocinnamate. Moreover, no coprostanol compounds have been found which exhibit a cholesteric phase⁴.

The importance of the planar structure of the cholesteryl molecule in forming the cholesteric liquid crystal may be further confirmed by observing the cholesteryl esters of the omega-substituted phenyl-alkyl-monocarboxylic acids. These esters, listed in Table I.1

Table I.1 -- Varying Chain Lengths and Cholesteric Phases of Cholesteryl Esters

Cholesteryl Ester	Number of Carbon Atoms	Phases
Benzoate	0	Cholesteric at melting point--red scattering
Phenyl Acetate	1	No cholesteric phase
Hydrocinnamate	2	Cholesteric phase--green at melting point
Phenyl Butyrate	3	No cholesteric phase
Phenyl Valerate	4	Cholesteric phase--blue at melting point
Phenyl Hexanoate	5	No cholesteric phase

have the following configuration:



These esters were prepared from the acid chlorides and cholesterol. The acids became increasingly difficult to obtain as the number of carbons in the alkyl side chain was increased. Cholesteryl benzoate and the esters containing an even number of carbon atoms in the substituting alkyl chain of the original acid chlorides, all exhibit a strong cholesteric phase. By examining the configuration of cholesteryl benzoate, it was apparent that the benzene ring continues the planar configuration of the cholesteryl ring. This conclusion became more evident upon examination of Taylor-Hirschfelder atomic models. The repetition of the results indicated that the alkyl chain is probably extended, for if it were randomly arranged, it should have made no difference whether the benzene ring was removed from the cholesteryl ring system by an odd or an even number of carbon atoms.

I.4 TEMPERATURE MEASUREMENTS

The measurement of the temperature dependence of the cholesteric colors has been of great benefit in the study of the various effects of molecular structure. To make this measurement, an aluminum block has been attached to a thermoelectric unit. See Figure I.3. The block can be cooled or heated so that a wide range of temperatures is available. The temperature of the block can be measured by a thermocouple or it can be recorded on the y axis of an x-y recorder using an enclosed thermistor. In operation, a film of liquid crystal is placed on a thin Mylar film in intimate contact with the block and illuminated with a gas discharge lamp. The reflection from the liquid crystal is monitored using a photomultiplier. The output of the photomultiplier is recorded as a function of temperature on the recorder.

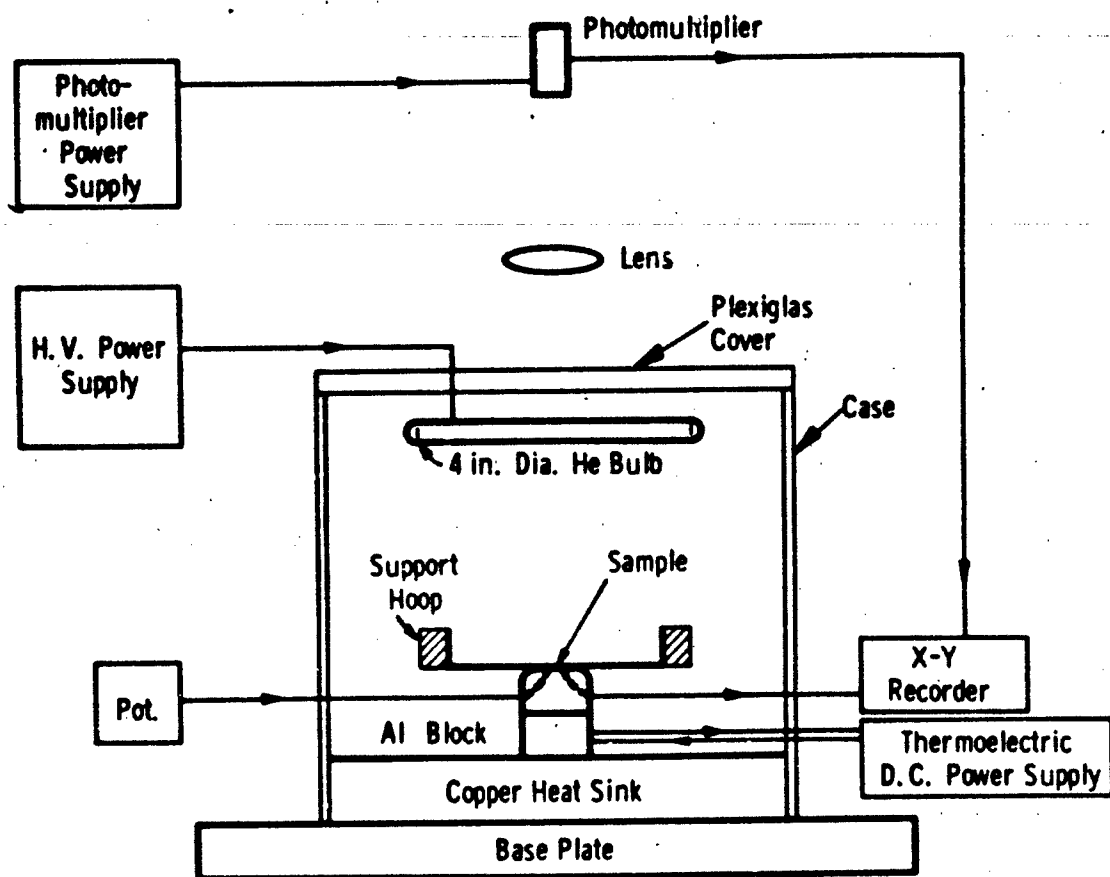


Figure 1.3 - Apparatus for measuring the temperature sensitivity of cholesteric liquid crystals.

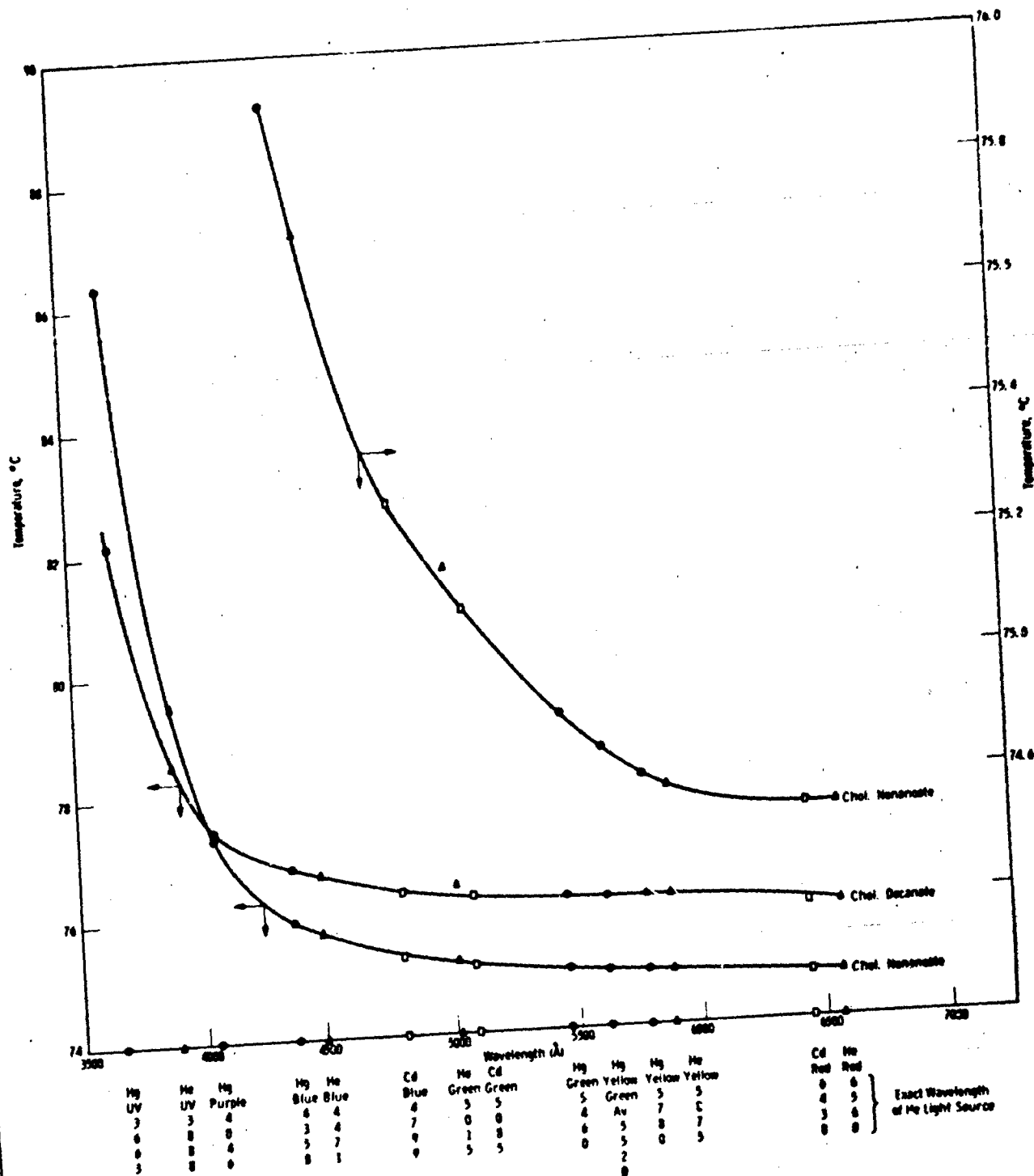


Figure I.4 - Temperature as a function of wavelength for cholesteryl nonanoate and cholesteryl decanoate.

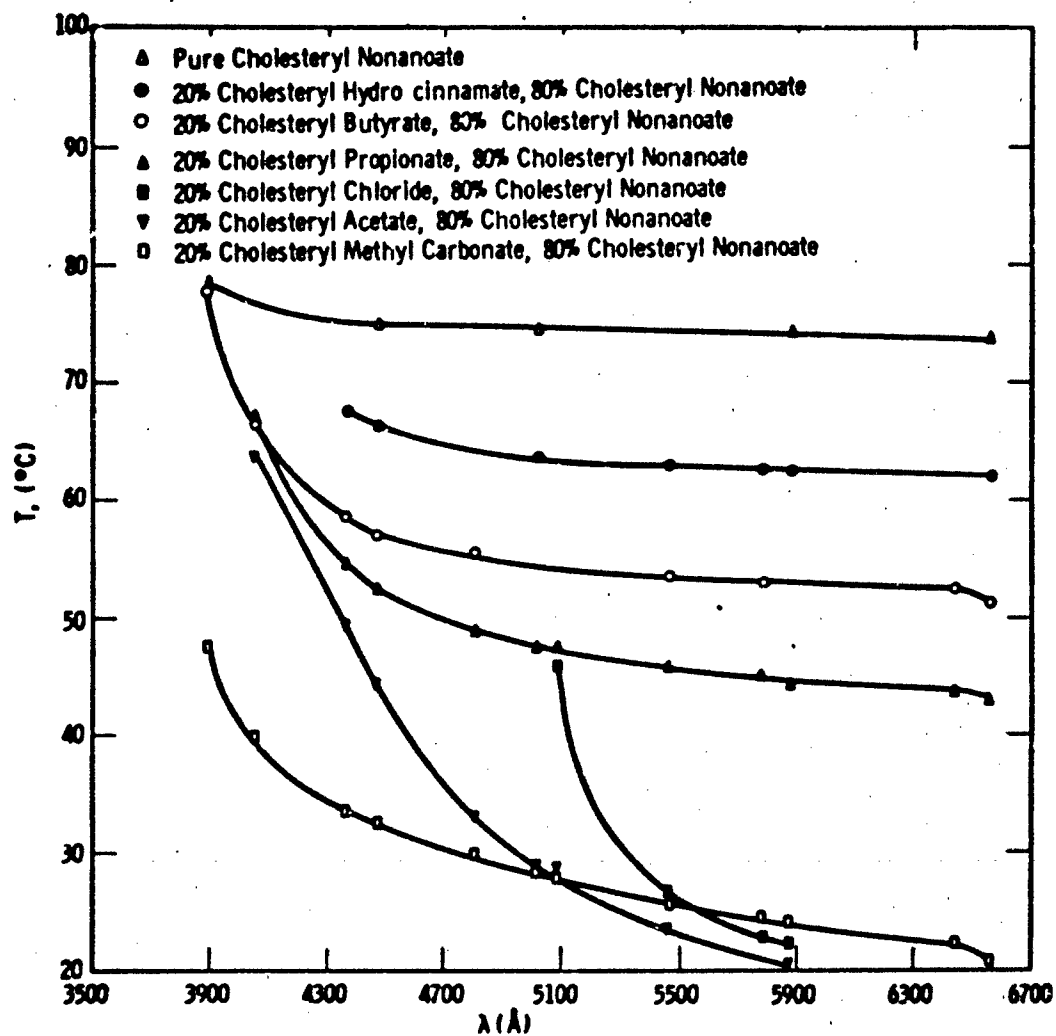


Figure 1.5 - Temperature as a function of wavelength for a number of cholesteric materials added to cholesteryl nonanoate.

The discharge lamps have specific wavelengths of maximum intensity which are recorded as peaks on the x-y plot. The temperature at which these peaks occur give sufficient information for a temperature vs dominant wavelength plot. See Figures I.4 and I.5.

The first use of this apparatus was to determine the effect of changes in structure when they involved only a small percentage of a mixture of cholesteric materials. Cholesterol nonanoate was used as a standard material and a number of both derivatives of cholesterol and fat soluble materials were added to it. Unless otherwise specified all percentages given in the appendices are by weight. In Figures I.5 and I.6 we see the effect of adding cholesterol esters of differing chain length. In this case one observes the shift in temperature sensitivity as a function of chain length. A change in chain length is readily identified by a change in the slope of the temperature vs wavelength curve. In Figure I.6 we see the results of adding derivatives of cholesteryl which vary either in the position of carbon atoms, as in the case of the cholesteryl butyrate and the cholesteryl isobutyrate, or in the number of hydrogen atoms as in the case of cholesterol butyrate and cholesterol crotonate. In all cases a clear and distinct difference is seen in the temperature vs wavelength characteristic. Note that not only are the four curves displaced vertically with respect to each other, but at any wavelength they have significantly different slopes. This is illustrated by Figure I.7. In Figure I.8 we see the effect of the addition of various oil soluble materials to a mixture of 80% nonanoate cholesteryl and 20% propionate. In this case we do not see as distinct a change in the slope of the temperature vs wavelength curve as we do in the temperature displacement. From this data, it becomes clear that there are two distinct identifying features which might allow for the recognition of a change in structure in the cholesteric phase, and which would be recognizable as a change in color at a particular temperature. One is a change in slope of a temperature vs wavelength curve and another is a translation of the temperature versus wavelength curve.

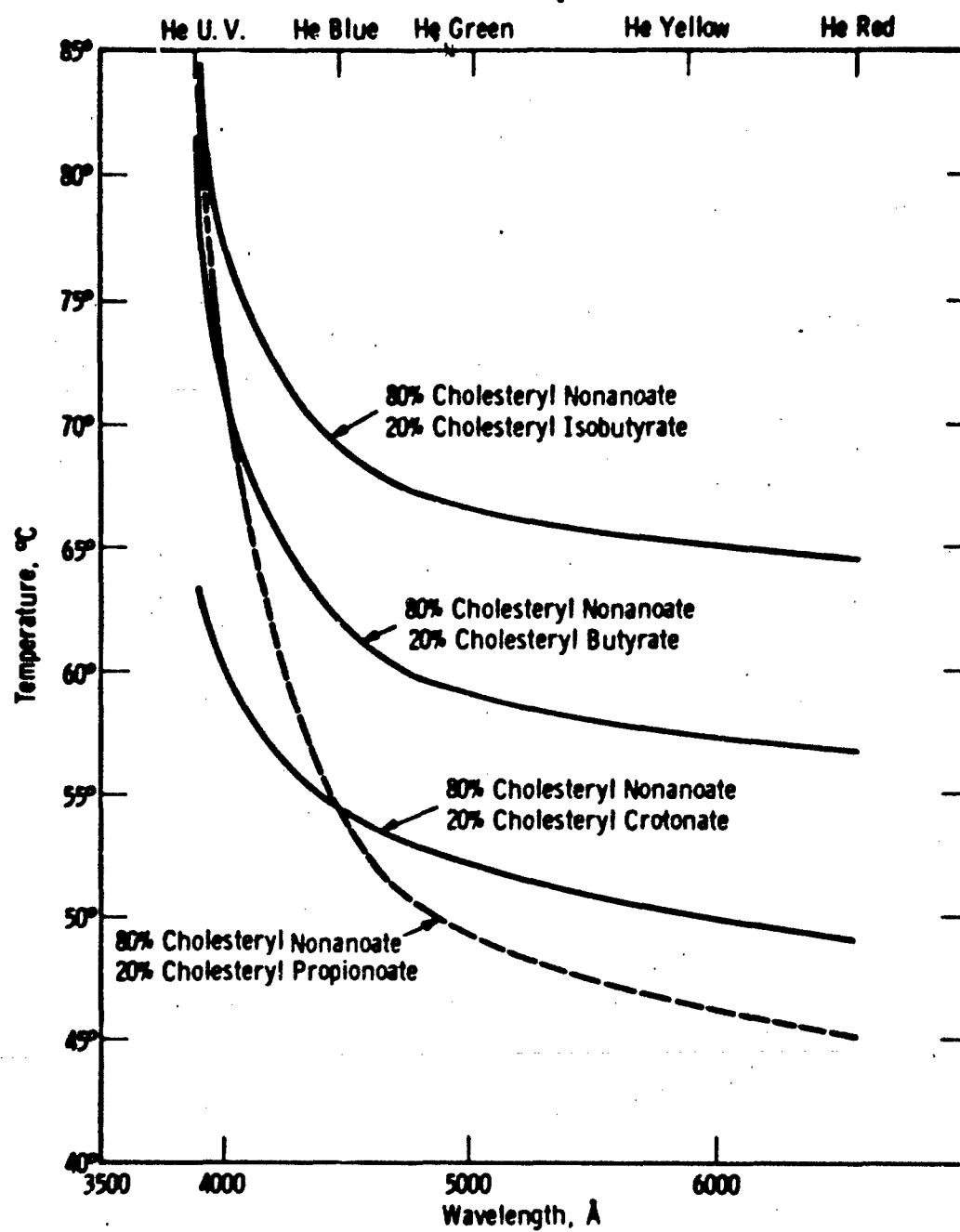


Figure I.6 - Temperature vs wavelength of four closely related materials added to cholesteryl nonanoate.

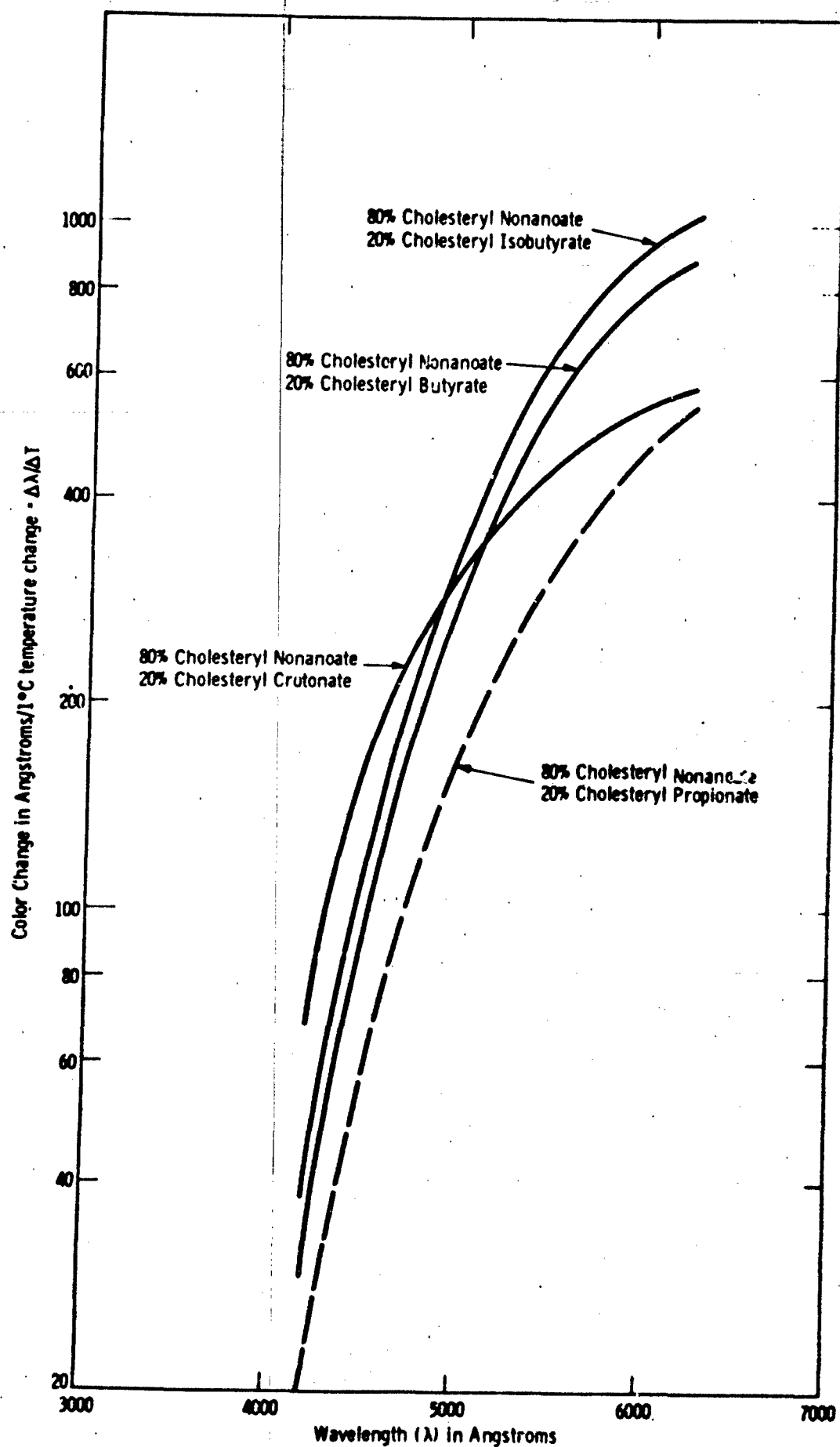


Figure 1.7 - Temperature sensitivity of Figure A.6 materials.

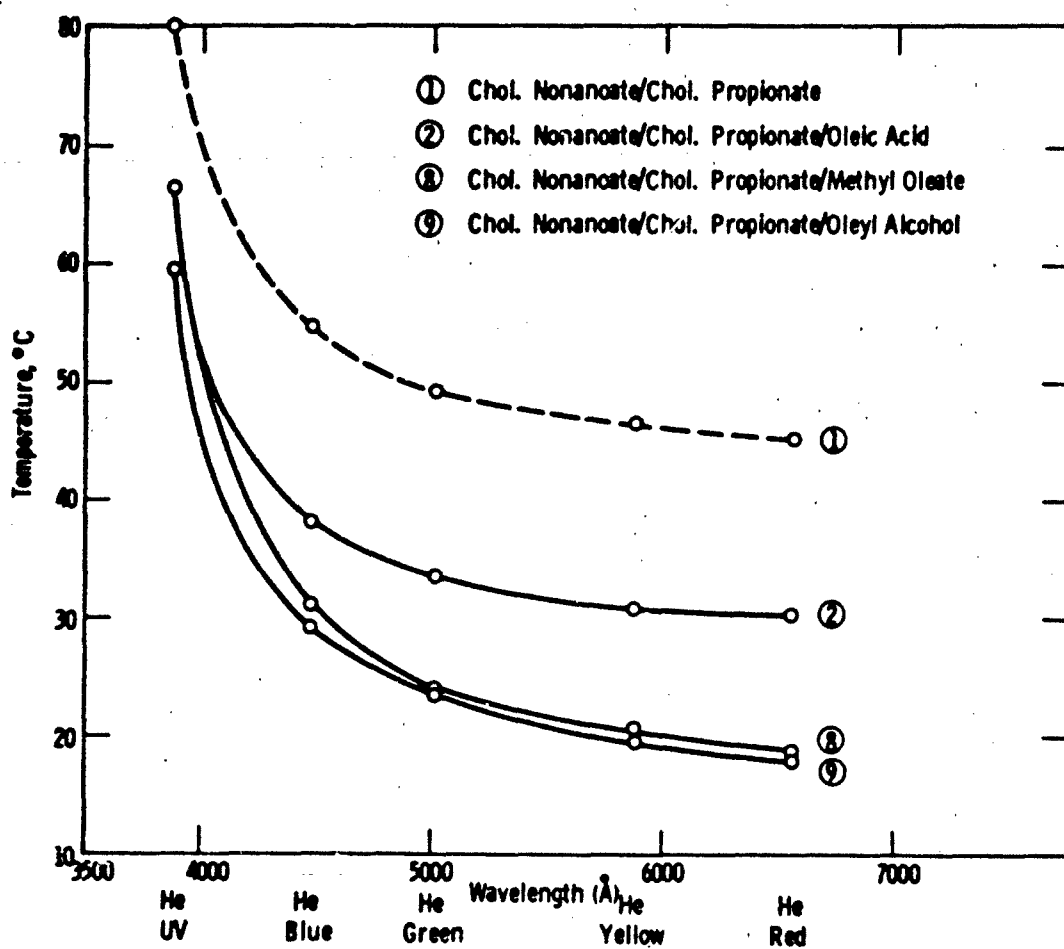


Figure I.8 - Temperature vs wavelength for liquid crystal material containing several oil soluble additives.

In many cases we would expect that both of the above effects would be operative. Thus, a reactive material may: (1) change the structure of some constituent of a liquid crystal, (2) remove from a liquid crystal some constituent which strongly affects its temperature vs wavelength characteristic, or (3) change the composition by the catalysis of a reaction. In the following discussions it will be shown how all of these effects were used to detect and discriminate between various types of vapors.

1.5 TEMPERATURE SENSITIVITY IN GAS DETECTION

In the preceding section the temperature sensitivity was seen to be sharply dependent on the type of additive to the liquid crystal material. In Figure 1.5 the material containing cholesteryl acetate is much less sensitive than the material containing cholesteryl propionate. By finding the proper additive, the temperature sensitivity of liquid crystal systems can be greatly decreased. An example of a stable additive which accomplished this purpose is cholesteryl chloride. In Figure 1.9 the temperature vs wavelength curves are plotted for several different mixtures of cholesteryl chloride in cholesteryl nonanoate. In a large temperature region (50°C), the 25% cholesteryl chloride is temperature insensitive. In this range a change in percent of cholesteryl chloride is very easily seen as a change of color. Any material which acts similar to cholesteryl chloride may be expected to behave in the same way. Examples of materials in this category are: cholesterol, cholesteryl bromide and, to a lesser degree, cholesteryl chloroformate. Table 1.2 gives the changes in color for various polar and non-polar solvents. The effect of polar solvents is a shift to the red, while the addition of a non-polar vapor shifts the color toward blue. However, in some instances there is a tendency not to change the color at all (note the effect of trichloroethylene at 20%). This indicates that we might expect some materials which, when added, will not appreciably change the color of the liquid crystal. It has been found that materials which have strong effects on the slope of the temperature vs wavelength curve tend to have a strong effect on this system while

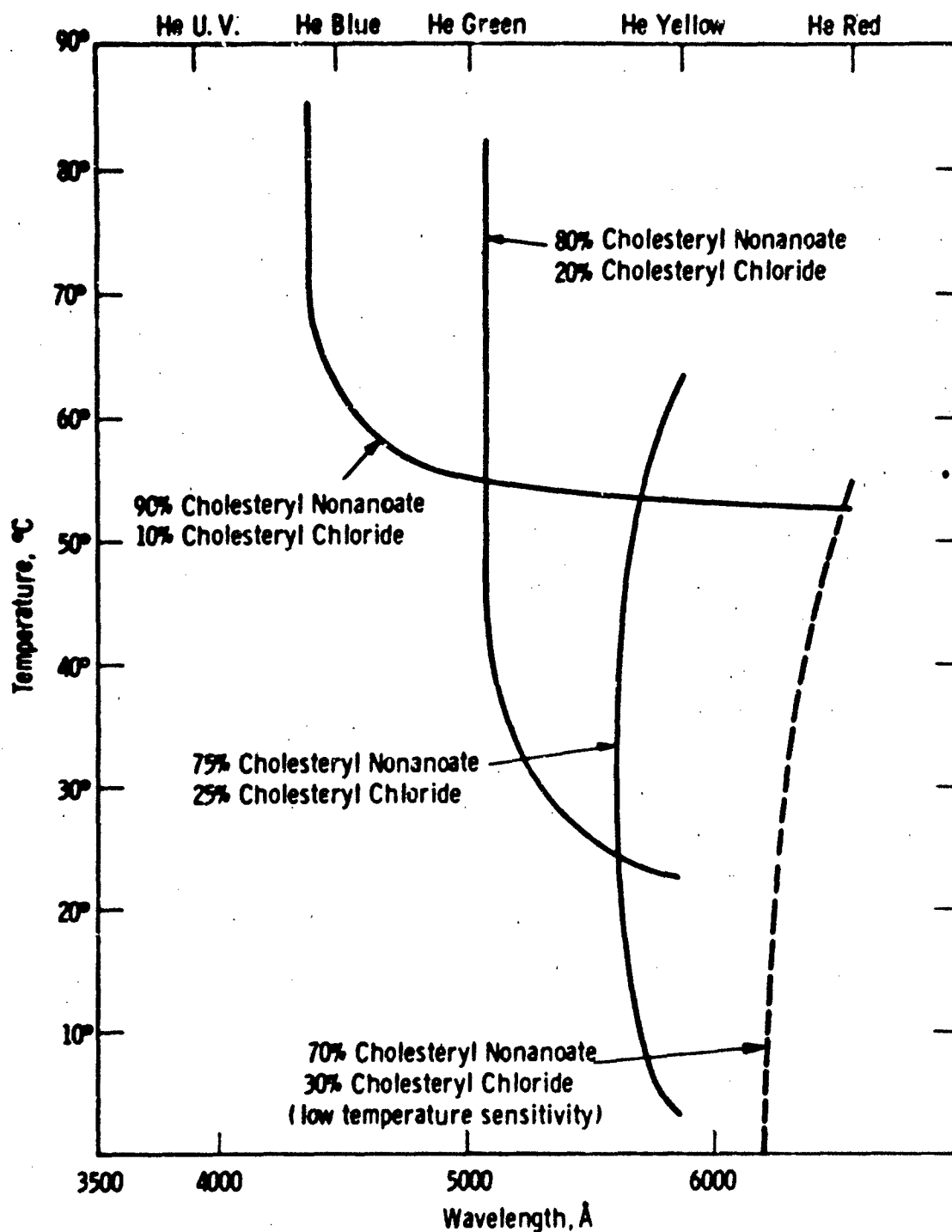


Figure I.9 - Temperature characteristics of cholesteryl chloride and cholesteryl nonanoate mixtures in various proportions.

Table I.2 - Response of Liquid Crystals to Various Solvent Vapors.

<u>Cholesteryl Chloride</u>	<u>Cholesteryl Nonanoate</u>	<u>Cholesteryl Oleate</u>	<u>Original Color</u>	<u>Solvent Vapors</u>	<u>Changed to</u>
15%	80%	5%	Red	Acetone Benzene Chloroform Trichloro- ethylene Methylene Chloride Petroleum Ether	Blue Blue Blue Blue Blue Blue Blue
20%	80%		Green	Benzene Chloroform Trichloro- ethylene Methylene Chloride Petroleum Ether	Blue Red No change Red Blue
25%	75%		Yellow- Red	Benzene Chloroform Trichloro- ethylene Methylene Chloride Petroleum Ether	Deeper red Red Deeper red Red Blue
30%	70%		Red	Chloroform Methylene Chloride Petroleum Ether	Deeper red Deeper red Blue

additives, whose main effect is to change the temperature at which the effect occurs, do not change the color greatly. In this category are many of the materials derived from oleic acid. A change in the molecular structure of these materials will have a much stronger effect on the temperature at which a color occurs than on the shape of the temperature vs wavelength curve (Figure I.4). This is not generally true of most reactive derivatives of cholesterol which may produce substantial changes in the shape of the temperature vs wavelength curve (Figure I.5).

In most cases the effect of a particular material on a temperature insensitive liquid crystal to which it is added may be obtained by examining a temperature sensitive system. In addition, a material which is temperature sensitive gives much more information concerning the effect of additives than a temperature insensitive material. Thus, the order of experiment has been: (1) to determine a reaction which will occur in liquid crystal systems, (2) to incorporate this reaction into a material which will form a temperature sensitive liquid crystal suitable for measuring the effects of this reaction, (3) to determine which of the materials is most suitable for spot testing.

I.6 EFFECT OF THICKNESS

In this study the thickness of the liquid crystal was maintained at as near 25 μ as possible. The variation of thickness of film is important for several reasons:

(1) The brightness varies with thickness. The equation for the scattering is of the following form:

$$I_r = I_o \left[1 - e^{-(\beta t)f(\lambda, T)} \right]$$

where t = thickness

I_r = the intensity of the reflected light

I_o = the intensity of the incident light

- e = the natural logarithmic base
- β = Beer's Law constant for the material which is about 5×10^2 cm^{-1} for most liquid crystals
- $f(\lambda, T)$ = a gaussian function of the wavelength and temperature for any specific material

When two materials are mixed together the effect is usually to alter β . However, in the liquid crystal case, the $f(\lambda, T)$ is altered with respect to T .

(2) The diffusion rate of a gas into a material is a function of thickness; the thicker a sample the longer the diffusion path and thus the slower the reaction procedures and the greater the quantity of the reactive gas needed. The quantity of gas needed to give a signal increases directly with the thickness of the film and the rate of reaction varies inversely with the square of the thickness.

Considering both factors, for any detectors there will be an optimum thickness for any gas concentration and exposure time. To obtain a film of liquid crystalline material of the desired thickness, the materials were weighed and dissolved in a petroleum ether-chloroform solvent system (this was subject to variation depending on the type of materials used). A 7 to 1 volume ratio of solvent to material was maintained. In practice, this gives approximately a 25μ film when cast on Mylar (as determined gravimetrically). In practice, a film 7 to 8μ might be desirable in order to increase the sensitivity, but a thinner film would not be suitable because of a lack of brightness.

I.7 REFERENCES

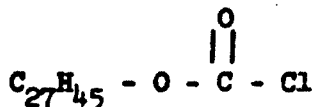
1. C. Oseen, Trans. Faraday Soc., 29:883 (1933)
2. H. deVries, Acta Cryst., 4:219 (1951)
3. L. Fieser and M. Fieser, Steroids, Reinhold (1959).
4. C. Wiegand, Zeitschrift Fur Naturforschung, 4b:249.

Appendix II
CHEMICAL PREPARATION OF MATERIALS

Unless otherwise specified all reactions were performed in a 3-necked flask fitted with ground glass joints and equipped with a stirrer, addition funnel, reflux water condenser, and drying tubes. Heat was applied by means of a variac controlled heating mantle. In those instances where some of the starting materials and/or the end products were subject to atmospheric oxidation, the reactions were performed in a dry nitrogen atmosphere maintained by means of a nitrogen delivery tube. This delivery tube (sparge tube) was placed so that the end of the tube was always below the liquid level in the flask. All solvents used were of highest purity or were freshly distilled.

All melting point determinations were made in capillary tubes and are reported uncorrected. To facilitate depicting structural formulations for the following materials, the cholesteryl moiety will be shown as $C_{27}H_{45}-$.

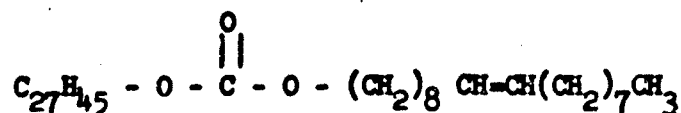
(1) Cholesteryl Chloroformate



Phosgene gas ($COCl_2$) was slowly bubbled through a solution of 250 g of cholesterol (Merck & Co.) dissolved in 2500 ml of anhydrous ethyl ether. After 8-10 minutes a white precipitate started to form, after an additional 20 minutes the precipitate started to dissolve, and after 10 minutes more the entire content of the flask was in solution. The phosgene delivery was discontinued and the reaction mixture was allowed to stand for 2-1/2 hours with continual stirring. The ether was removed by vacuum distillation and the white crystalline residue was

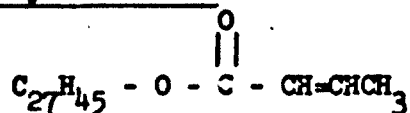
washed with acetone and recrystallized. Fine, white needles were obtained melting at 118.5°C (from acetone).

(2) Cholesteryl Oleyl Carbonate



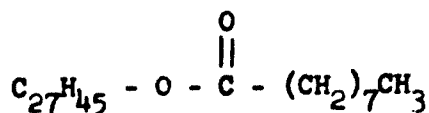
To cholesteryl chloroformate (224.6 g, 0.5 mole) dissolved in 400 ml of dry benzene was added, a drop at a time, a solution of 136.9 g (0.51 moles) oleyl alcohol (Archer-Daniels-Midland) and 29.6 g (0.50 moles) freshly distilled pyridine dissolved in 200 ml dry benzene. A slight exotherm was noted during the addition. After complete addition, the contents of the flask were heated to and maintained at the temperature of reflux for 1 hour. After cooling the solution was filtered and methyl alcohol added to the filtrate until further addition caused no turbidity. By means of a separatory funnel the oily layer was removed and washed repeatedly with methanol until a liquid crystal color temperature of 21.0°C to 22.5°C was obtained.

(3) Cholesteryl Crotonate



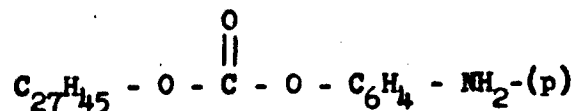
To a benzene (250 ml) solution of 96.6 g (0.25 moles) of cholesterol and 20.6 (0.26 moles) of pyridine, was added, dropwise, 27.2 g (0.26 moles) of crotonyl chloride dissolved in 35 ml benzene. A strong exotherm resulted. After cooling the mixture and filtering, methanol was added to the filtrate. The solid precipitate that formed was washed with alcohol and then recrystallized from ethanol to give white crystals which started softening at 90°C and were completely molten at 103°C. These results are in accordance with values found in the literature.

(4) Cholesteryl Nonanoate.



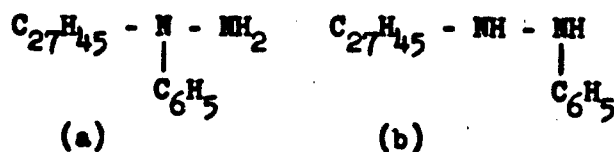
To 463.9 g (1.2 moles) cholesterol and 200.0 g (1.13 moles) nonanoyl chloride dissolved in 950 ml benzene, was added, dropwise, 89.4 g (1.13 moles) pyridine dissolved in 100 ml benzene. An exotherm was noted. After complete addition the reaction mixture was heated to and maintained at the reflux temperature for 1.0 hour, cooled, and then filtered. The filtrate was treated with methanol to obtain a crystalline product which when recrystallized from acetone had a melting point of 79.3° - 80°C and a clearing point of 91.8° - 92°C.

(5) Cholesteryl p - Aminophenyl Carbonate.



A heterogeneous solution of 7.28 g (0.05 moles) p - aminophenol hydrochloride and 22.4 g (0.05 moles) cholesteryl chloroformate in 150 ml benzene was refluxed for 1 hr. A solution of 7.9 g (0.1 moles) pyridine in 20 ml benzene was added dropwise with the effect that the insoluble p - aminophenol hydrochloride dissolved and the insoluble pyridine hydrochloride formed. After complete addition, reflux was continued for an additional 2.0 hours. The filtrate was cooled, filtered, and treated with methanol. The product obtained was recrystallized from acetone and had a melting point of 223°C.

(6) Cholesteryl Phenylhydrazine.



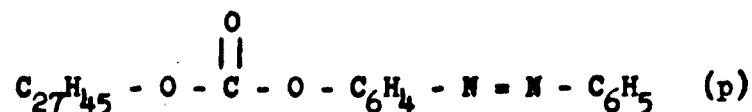
The structure of this compound has not been completely elucidated as to whether it is (a) or (b). The older literature prefers structure (a). A mixture of 8.1 g (0.02 moles) cholesteryl chloride (Aldrich Chemical Co.) and 25 ml phenylhydrazine was heated to and maintained at reflux temperature for 2.5 hours. After cooling, the solid reaction mixture was treated with benzene to dissolve the product and filtered to remove the phenylhydrazine hydrochloride salt. The filtrate was treated with methanol to obtain a solid material which when recrystallized from benzene and washed with methanol had a melting point of 198 - 199°C.

(7) N-Cholesterylaniline.



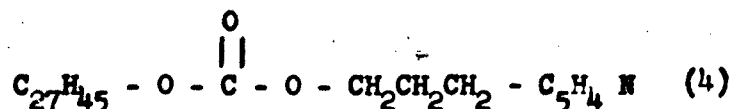
A mixture of 8.1 g (0.02 moles) cholesteryl chloride and aniline (25 ml) was heated to and maintained at reflux temperature for 2.5 hours. After cooling, benzene was added to dissolve the product and the aniline hydrochloride salt was removed by filtration. The filtrate was treated with methanol, and the solid obtained was recrystallized from a benzene/methanol mixture to give crystals melting at 189-190°C.

(8) Cholesteryl p - Phenylazophenyl Carbonate.



A flask was charged with 22.5 g (0.05 moles) cholesteryl chloroformate, 10.0 g (0.05 moles) p - phenylazophenol, 3.9 g (0.05 moles) pyridine, and 150 ml benzene. The reaction mixture was heated and maintained at reflux temperature for 2.0 hours and then cooled, filtered, and the filtrate treated with methanol. The product obtained was recrystallized from benzene/methanol solution and exhibited a melting point of 166° - 167.5°C.

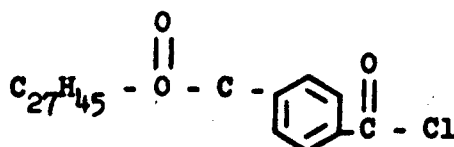
(9) Cholesteryl 3 - (4-Pyridyl) - Propyl Carbonate.



To 6.86 g (0.05 moles) 4-pyridine propanol dissolved in acetone, was added, dropwise, concentrated hydrochloric acid until addition no longer produced any turbidity. The oily layer that formed was separated and washed repeatedly with acetone and then subjected to a vacuum to remove the acetone. This product, 4-pyridine propanol hydrochloride, was charged in a flask along with 3.9 g (0.05 moles) pyridine and 150 ml benzene. The heterogeneous system was then, dropwise, treated with 22.4 g (0.05 moles) cholesteryl chloroformate dissolved in 50 ml

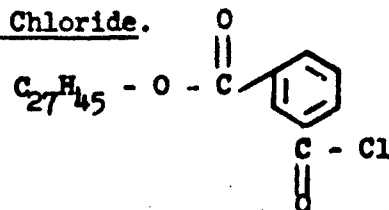
benzene. A slight exotherm was noted as well as a change in the color of the solution (reddish orange). The reaction mixture was maintained at reflux temperature for 2.0 hours, cooled, filtered, and the filtrate washed with a 5% sodium carbonate solution. The benzene solution was treated with methanol and a material was obtained which started to melt at 100°C but did not clear until 107°C.

(10) Cholesteryl Terephthalyl Chloride.



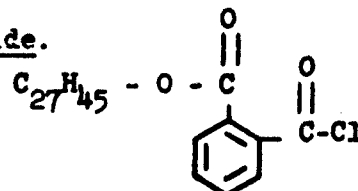
To 20.3 g (0.1 mole) terephthalyl chloride dissolved in 175 ml benzene, was added, dropwise, 38.6 g (0.1 mole) cholesterol, and 7.9 g (0.1 mole) pyridine dissolved in 150 ml benzene. The mixture was reacted at reflux temperature for 1.0 hour, cooled, filtered, and the solvent removed from the filtrate by means of reduced pressure. This product exhibited a melting point of 161° - 164°C.

(11) Cholesteryl Isophthalyl Chloride.



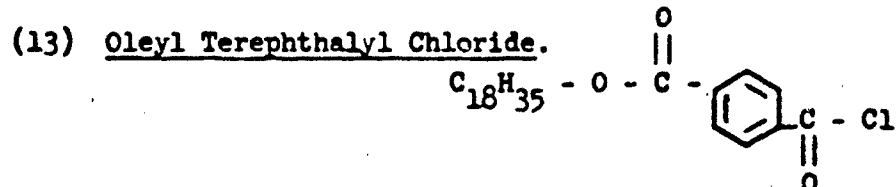
To 20.3 g (0.1 mole) isophthalyl chloride dissolved in 125 ml benzene, was added, dropwise, 38.6 g (0.1 mole) cholesterol and 7.9 g (0.1 mole) pyridine dissolved in 125 ml benzene. The mixture was reacted at reflux temperature for 1.0 hour, cooled, filtered, and the solvent was removed from the filtrate by means of reduced pressure. The product so obtained was an oil.

(12) Cholesteryl Phthalyl Chloride.

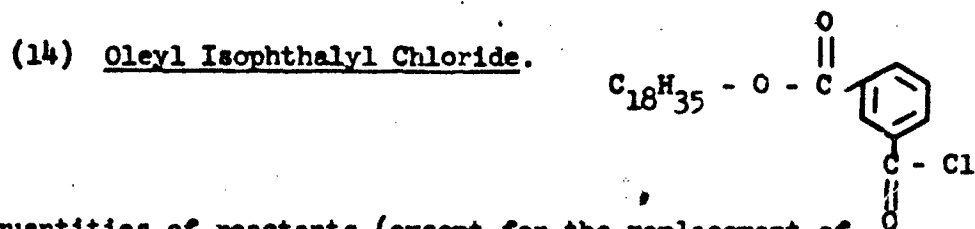


To 20.3 g (0.1 mole) phthalyl chloride dissolved in 125 ml benzene, was added, dropwise, 38.6 g (0.1 mole) cholesterol and 7.9 g (0.1 mole)

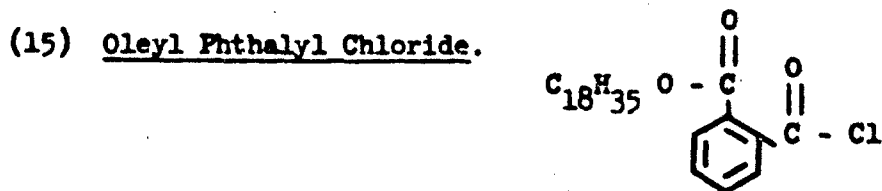
pyridine dissolved in 125 ml benzene. The mixture was reacted and the product isolated in the same manner as described above (11), to obtain an oil.



To 20.3 g (0.1 mole) terephthalyl chloride dissolved in 125 ml benzene, was added, dropwise, 26.9 g (0.1 mole) oleyl alcohol and 7.9 g (0.1 mole) pyridine dissolved in 100 ml benzene. The reaction mixture was heated to reflux temperature and the temperature maintained for 1.0 hour, and then cooled, filtered, and the solvent removed from the filtrate by means of reduced pressure. The product obtained was an oil which slowly crystallized on standing.

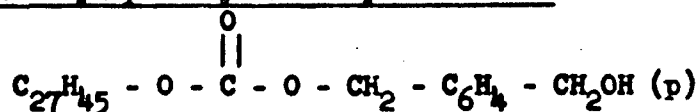


The same quantities of reactants (except for the replacement of terephthalyl chloride with isophthalyl chloride) and solvent were used as described in the previous preparation. The product, an oil which did not crystallize on standing, was obtained by the same procedures as outlined above (13).



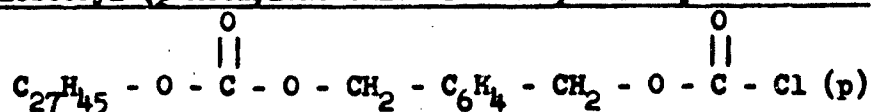
The same preparative procedures were used in this preparation as in (13) above with the exception that phthalyl chloride was used in place of terephthalyl chloride. The end product was an oil which did not crystallize on standing.

(16) Cholesteryl p-Methylol Benzyl Carbonate.



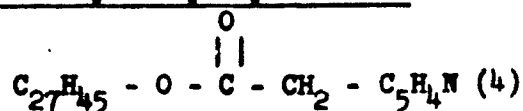
To 22.5 g (0.05 mole) cholesteryl chloroformate dissolved in 75 ml benzene, was added, a mixture of 6.85 g (0.05 mole) p-dimethylolbenzene and 3.9 g (0.05 mole) pyridine dissolved in 200 ml benzene. When the reaction mixture was heated, the dissolved p-dimethylolbenzene became soluble. The solution was refluxed for 1.0 hour and then allowed to cool. The product was not isolated but was used (in solution) for the following preparation.

(17) Cholesteryl (p-Methylene Chloroformate) - Benzyl Carbonate.



Continuing from the preceding preparation. (16), the reaction flask was equipped with a gas delivery tube extending below the surface of the solution. Phosgene gas (COCl_2) was passed into the flask at a rate of approximately 0.2 liters per minute for a period of 15 minutes. At the end of this period gas delivery was discontinued and the entire contents of the flask were refluxed for 1.0 hour. The reaction mixture was cooled, filtered, and the solvent removed using a reduced pressure. The solid that remained was washed with acetone several times. This crystalline material started melting at 171°C and was completely molten at 175°C .

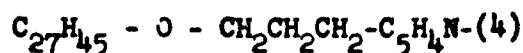
(18) Cholesteryl-4-Pyridyl Acetate.



To 15.5 g (0.04 mole) cholesterol in 75 ml xylene, was added, 7.0 g (0.04 mole) 4-pyridine acetic acid hydrochloride in 30 ml of xylene, and then 1 g of p-toluenesulfonic acid was added. The reactants were refluxed for 7.5 hours. The solvent was removed by vacuum

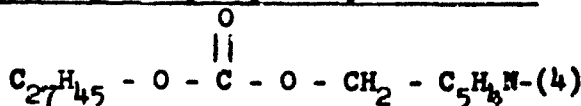
distillation and the solid product that was obtained was recrystallized from methanol, m.p. 148 - 149°C.

(19) Cholesteryl 3-(4-Pyridyl)-Propyl Ether.



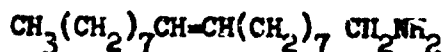
A flask was charged with 20.5 g (0.15 moles) of 4-pyridyl-1-propanol, 38.6 g (0.10 mole) of cholesterol, 90 g of activated Floridan Clay and xylene as the solvent. A nitrogen atmosphere was continuously maintained during the reaction. The reactants were refluxed for 2.0 hours. After cooling and filtering, methanol was added to the filtrate and a product was obtained. This product was found to be unreacted cholesterol, m.p. 147° - 148°C alone and when mixed with an authentic sample. Only a minute amount of a solid material believed to be the desired product was isolated. It was used as obtained and was not purified further.

(20) Cholesteryl 4-Pyridylmethyl Carbonate.



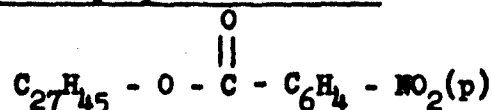
To 67.38 g (0.15 mole) cholesteryl chloroformate dissolved in 125 ml benzene was added a drop at a time a solution of 16.35 g (0.15 mole) 4-pyridyl carbinol and 18.2 g (0.18 mole; 20% excess) triethylamine dissolved in 125 ml benzene. (Note: the carbinol was not completely soluble.) During the addition the solution became red in color and an exotherm was noted. Another 100 ml of benzene was added to decrease the viscosity of the solution which was then refluxed for 1.0 hour. Some difficulties were encountered trying to isolate and purify this product. It was used in this impure state as a test reagent. Since the results were not encouraging, no further purification was attempted.

(21) Oleyl Amine.



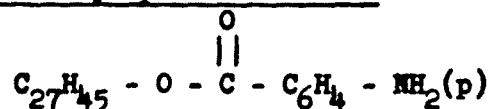
This material was obtained from Armour Chemical Co. as Armeen OD. It was not used as such but vacuum redistilled. The material that came off at 126°C at 0.06 mm pressure was labelled and used as oleyl amine.

(22) Cholesteryl p-Nitrobenzoate.



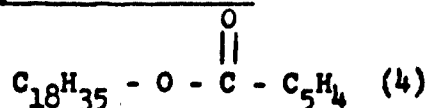
To 293.8 g (0.76 mole) cholesterol and 59.3 g (0.75 mole) pyridine dissolved in 500 ml benzene, was added, dropwise, 139.2 g (0.75 mole) p-nitrobenzoyl chloride dissolved in 400 ml benzene. A strong exotherm resulted during the addition. The mixture was refluxed for 2.0 hours, the hot solution was filtered and then allowed to cool. A tan crystall solid was obtained which was recrystallized from methyl cellosolve (ethylene glycol monomethyl ether). The recrystallized solid was pale yellow in color and melted at 190 - 191°C.

(23) Cholesteryl p-Aminobenzoate.



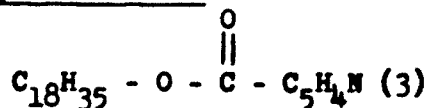
The cholesteryl p-nitrobenzoate prepared above, (22), was used for this preparation. Thus, to 6 g of the p-nitro derivative in 80 ml glacial acetic acid was added 3.5 g of 100 mesh iron filings. The mixture was boiled under gentle reflux. The solution went from colorless to dark brown during the first half-hour, and after 1.5 hours all of the p-nitro compound had dissolved. Reflux was maintained for a total of 2.5 hours. The solution was transferred to a beaker and allowed to cool (crystallized). The entire contents of the beaker were repeatedly washed with 1 N hydrochloric acid until the washings were colorless, and then with water until the washings were neutral to litmus. The solid so obtained was recrystallized twice from boiling amyl acetate to give large tan needles with a melting point of 238 - 239°C.

(24) Oleyl Isonicotinate.



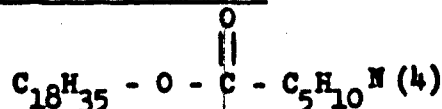
To 20.5 g (0.17 mole) isonicotinic acid, was added, 80 ml (excess) of thionyl chloride (SOCl_2) and the mixture refluxed for 2.0 hours. At the end of this period, the flask was set up for a distillation, and the excess thionyl chloride removed by distillation. The reflux condenser was returned to the flask which now contained isonicotinoyl chloride. After adding 100 ml of benzene to the flask, 91.5 g (0.341 moles) of oleyl alcohol dissolved in 100 ml benzene was added dropwise. During the addition the reaction flask was kept in an ice bath. After the addition was completed, the flask was allowed to warm up and then heated and maintained at reflux temperature for 30 minutes. The contents of the flask were cooled, treated with 250 ml of a 20% sodium carbonate solution for 15 minutes, transferred to a separatory funnel, and the aqueous layer discarded. The benzene phase was washed with water and dried over Drierite. The solvent was distilled and the residue fractionally distilled. In this manner oleyl isonicotinate (b.p. 190 - 193°/0.11 mm and 179 - 182°/0.06 mm) was obtained.

(25) Oleyl Nicotinate.



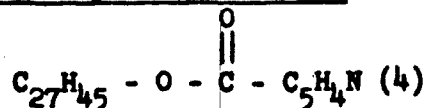
Nicotinoyl chloride (17.8 g, 0.1 mole) was dissolved in 150 ml benzene and the flask cooled in an ice bath. Oleyl alcohol (26.8 g; 0.1 mole) in 100 ml benzene was added dropwise. After complete addition, the reaction mixture was heated to, and maintained at, reflux for 2.0 hours. The reaction mixture was cooled, treated with 150 ml of 20% sodium carbonate solution (added slowly), transferred to a separatory funnel, and separated. The benzene layer was distilled at atmospheric pressure to remove solvent and then under reduced pressure to obtain the oleyl nicotinate, b.p. 191°C/0.07 mm. Hg.

(26) Oleyl Isonipecotoate.



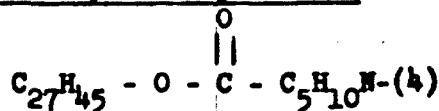
This material was prepared in a manner similar to that used in the preparation of oleyl isonicotinate (24). Thus, 20.5 g (0.16 mole) isonipecotic acid, 80 ml (excess) thionyl chloride, and 42.7 g (0.16 mole) oleyl alcohol were used in this preparation. Vacuum distillation resulted in obtaining oleyl isonipecotoate, b.p. 130°C/0.1 mm.Hg.

(27) Cholesteryl Isonicotinate.



As in the preparation of oleyl isonicotinate (24), isonicotinoyl chloride was first prepared from 20.5 g (0.17 moles) isonicotinic acid and 80 ml (excess) of thionyl chloride. This product was then reacted with 64.3 g, (0.17 moles) cholesterol in 300 ml benzene. To the flask was added 200 ml of a 20% sodium carbonate solution, and the contents of the flask were then separated in a separatory funnel. The benzene phase was treated with methanol and the solid so obtained by filtration was recrystallized from acetone, m.p. 172.5 - 173°C.

(28) Cholesteryl Isonipecotoate.



Isonipecotoyl chloride was prepared from 20.5 g (0.16 moles) isonipecotic acid and 80 ml thionyl chloride. This product was then reacted with 61.4 g (0.16 mole) cholesterol in 325 ml benzene. Using the same procedures as in the preparation of cholesteryl isonicotinate (27) for obtaining the product from the reaction mixture, an oil was obtained. Upon standing, this oil crystallized partially. Attempts to recrystallize this oil have been only partially successful. Usually it comes out of

solution as an oil first and then slowly crystallizes to give a solid which starts to melt at 81°C and is completely molten at 89°C.

Appendix III
VOLUMETRIC DILUTION APPARATUS

The volumetric dilution apparatus shown in Figure III.1 consisted, very briefly, of a 3 cc sample chamber A connected at one end to a manometer (B), to the gas bottle (C) and to the atmosphere (D). At the other end this sample chamber (A) is connected to a vacuum line (E) and to a mixing volume (F) which, in turn, is connected to a smaller reaction chamber (G) that can be evacuated independently.

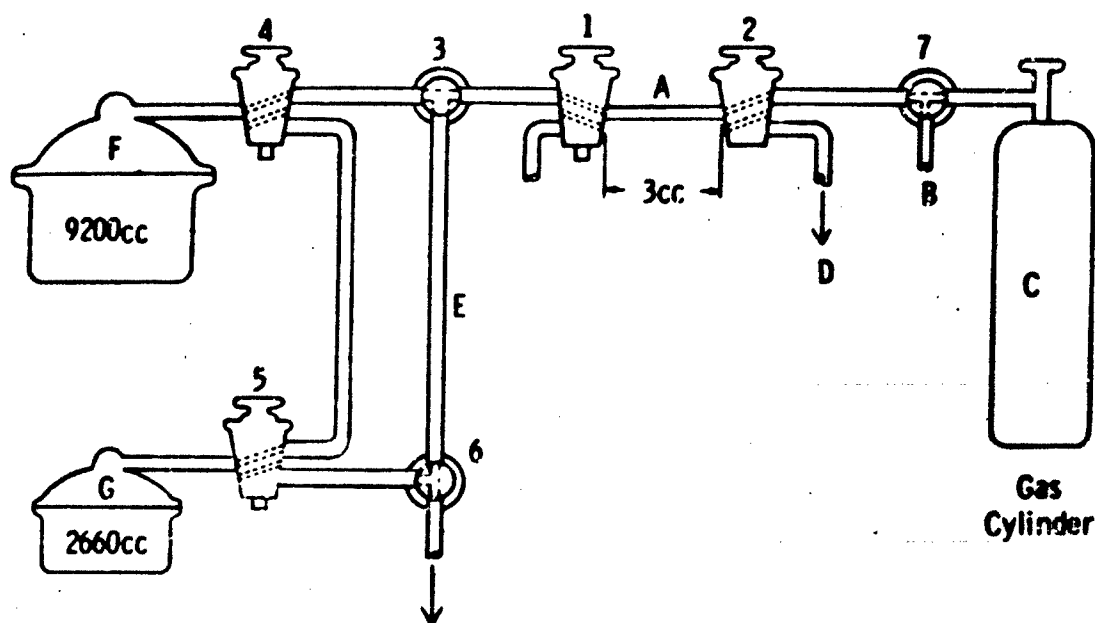


Figure III.1 - Volumetric dilution apparatus.

The test sample hoop is placed in (G) and the whole system is evacuated to a known pressure (usually less than 4 mm Hg) up to the gas bottle. After checking for leaks, three-way stopcock 1 is closed and three-way stopcock 2 is open to the manometer and the gas bottle. A known pressure of gas is then bled into sample chamber (A); when this is done stopcock 2 is also closed, so that sample chamber (A) contains 3 cc of contaminant gas at a known pressure. Stopcock (3) is rotated 180° so it is open from (A) to (F) but closed to (E). Stopcocks 1, 2 and 4 are subsequently turned so as to allow atmospheric air to flush the contaminant gas into mixing volume (F). In this manner 3 cc of gas at any desired pressure is mixed with 9200 cc of air to atmospheric pressure, yielding the desired contaminant gas/air volume ratio. The diluted gas in volume (F), with or without a delay of five minutes, is then allowed to flow into the evacuated reaction chamber (G), where the test hoop is. When pressure equilibrium between (F) and (G) is established, the test hoop is exposed to the desired concentration of contaminant gas at a pressure (usually about 570 torr) somewhat below atmospheric pressure. The latter may be attained either by bleeding air into (F) and repeating the procedure described above or by bleeding air into (G) directly. In either case the contaminant gas concentration is reduced somewhat by a predictable amount. With this method, concentrations as low as 6 parts per million have been obtained, with even lower concentrations possible.

The ratio between the amount of detecting material spread out on the Mylar hoop (4.25 inch diameter) and the actual amount of gas present in the test chamber during the experiment is large, especially at the low contaminant gas concentrations explored. Therefore, the contaminant gas concentration in the test chamber decreases during a 15 minute exposure because of continuous reaction with the liquid crystal materials. That is, the actual average concentration of contaminant gas over the duration of the test is perceptibly lower than the initial concentration reported in each case. Therefore, the shift in color temperature of the detecting material being investigated would most probably be somewhat greater if the contaminant gas concentration

were kept constant or if the ratio of reactive material to contaminant gas were greatly reduced.

After the desired length of exposure, the sample is removed and tested in the temperature versus wavelength measuring apparatus. Each sample is first tested before exposure to contaminant gas, then exposed and tested again, the whole operation taking about 1.5 hour.

Appendix IV

APPLICATION OF LIQUID CRYSTAL DETECTORS

The reactive materials delivered to the AF in accordance with the contract are very sensitive to small quantities of gases which are usually present in the laboratory atmosphere so they must be protected from premature exposure.

In making a sample for laboratory use, a thin film of the material must be prepared on a suitable substrate. This substrate may be any material which gives good liquid crystal alignment, but does not react with the liquid crystal. Suitable materials are epoxy coated metals and Mylar. Mylar is the most convenient material to use because it is available in a wide variety of sizes and thicknesses. Any convenient area of detector can be used. However, if a limited amount of contaminated air is being used for testing, the size of the detecting area used should be kept reasonably small, because otherwise enough of the contaminant will be absorbed during a 15 minute exposure to appreciably alter the concentration of the contaminant. If the area is made less than 3 mm in diameter then magnification will be required in order to observe color changes.

The film may be put down either by casting or spraying. Each of the materials is provided in a solvent which will allow casting of samples. If further dilution is desired, as for spraying, a solvent should be used. Eight parts by volume of solvent to one part liquid crystal will yield 20u to 25u film which is a desired thickness. The film can be cast using an eye dropper or hypodermic syringe. To allow the material to flow properly on the substrate, a few drops are placed in the center of the area to be covered. After this procedure, the solvent is allowed to evaporate. If any solvent remains the test may be

invalid. To spray a film the dilution of the liquid crystal is not critical. However, the skill of the operator becomes more important. When spraying this material, any desired shape or area may be covered and most commercially available air guns may be used. The material is usually applied in several coats to obtain the proper thickness.

The detectors may be exposed to gas at any temperature from 10°C to 80°C. They may be exposed at this wide range of temperature because the indicating reaction is not a function of the state of the material. The film may simply be exposed to static air that contains the gas to be detected. However, a flow of air across the film reduces the required exposure time.

The interpretation of the results of these tests may be made in some cases by directly noting a permanent change from green to red (see the section on UDMH) at room temperature. However, to use most of the test materials one needs to heat the reacted detector sample and note whether it shifts color at a higher or lower temperature than an unreacted sample. Heating can be easily achieved with electric current, a light bulb, a flame or even body heat. For quantitative analysis the amount of this temperature shift should be determined. Generally a pair of samples of each material should be prepared. One is used for a reference and is covered so that it will not react with the contaminant. After reaction the pair are heated until one turns red and then slowly heated further until the second turns red. The difference in color-shift temperature or "red temperature" is noted. A small change in the red temperature indicates a small concentration of contaminant while a large red temperature shift would mean a large concentration of contaminant. See Table 1.1. If the "red temperature" of the exposed material is higher than the red temperature of the unexposed material the color shift is said to be positive.

If accurate temperature indicating methods are not available a second technique can be employed. A pair of unexposed and exposed samples are heated together until the unexposed sample turns green.

The amount and direction of color shift of the other sample will indicate the type and amount of reaction. See Table 1.2. If a large concentration of the reactive gas is present and/or if the exposure time is long, then the exposed sample will appear black at the testing temperature. For materials that exhibit a positive critical temperature shift for some gases and a negative shift for others, the samples will have to be heated or cooled to determine whether the shift was positive or negative.

A third technique is to use a set of nonreactive standard materials that have temperature vs wavelength (color) characteristics that match those of the reactive sample after exposure to various gas concentrations. By comparing the reactive samples with these standards the amount of contamination can be determined.

Table IV.1 lists all of the samples delivered to RADC and indicates which gases will react with each. The color transition temperature will shift up or down upon exposure as indicated. Before exposure all of these materials have a transition temperature of about 29°C. The solvent used for materials numbered 3, 4, and 5 is petroleum ether. The solvent used for all of the other samples is 80% petroleum ether and 20% chloroform.

Two temperature insensitive materials were also supplied. These permanently shift color from green to red on exposure to UDMH or hydrazine. The composition by weight is as follows:

UDMH #1	2 parts	Cholesteryl Terephthalyl Chloride
	7 "	Oleate
	1 "	Chol. Nonanoate
	2 "	Chol. Chloride
UDMH #2	2 parts	Chol. Isophthalyl Chloride
	7 "	Cholesteryl Erucyl Carbonate
	1 "	Chol. Nonanoate
	2 "	Chol. Chloride

Table IV.1 - List of Reactive Materials Supplied

Detector	Matrix Composition C. Non./OCC*	Detector %	Direction of Color Shift				
			NO ₂ + N ₂ O ₄	HNO ₃	HF + HCl	H ₂ H	UDMH
1. Methyl Linoleate	60/40	3.4	down				
2. Methyl Linolenate	60/40	3.4	down				
3. Cholesteryl Phenyl Hydrazine	50/50	4		up			
4. Oleyl Isonicotinate	60/40	3.5		up	up		
5. Oleyl Amine	60/40	3.5		up	up		
6. Oleyl Chloroformate	60/40	3				up	down
7. Oleyl Terephthaloyl Chloride	54/46	4				up	down
8. Oleyl Isophthaloyl Chloride	56/44	4				up	down
9. Cholesteryl Iso- phthaloyl Chloride	40/60	4				down	down
10. Cholesteryl Ter- ephthaloyl Chloride	30/70	4				first up then down	down
11. Oleic Acid	60/40	4.5		small down			

* C. Non. = Cholesteryl Nonanoate
OCC = Oleyl Cholesteryl Carbonate

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author) Westinghouse Electric Corporation Research Laboratories Pittsburgh, Pennsylvania		2a REPORT SECURITY CLASSIFICATION Unclassified	
		2b GROUP 3	
3 REPORT TITLE Reactive Materials			
4 DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Report			
5 AUTHOR(S) (Last name, first name, initial) Ferguson, J.L. Rush, R.S. Goldberg, M.H. Scala, L.C. Jones, C.H. Davis, F.			
6. REPORT DATE August 1965		7a. TOTAL NO. OF PAGES 110	7b. NO. OF REFS 19
8a. CONTRACT OR GRANT NO. AF30(603)-3306 A. PROJECT NO. 5534 c. Task 553402 d.		9a. ORIGINATOR'S REPORT NUMBER(S) 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) RADC-TR-64-569	
10. AVAILABILITY/LIMITATION NOTICES This report is releasable to CFSTI.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Rome Air Development Center Griffiss AFB, New York 13442	
13 ABSTRACT Cholesteric liquid crystals were developed to detect the presence of certain gases at concentration levels of 10 parts per million and less.			

DD FORM 1 JAN 64 1473

UNCLASSIFIED

Security Classification

UNCLASSIFIED

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Gas Detectors Steroids Cholesterol Contamination Atmospheric pollution						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (corporate author) issuing the report.

2a. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers (either by the originator or by the sponsor), also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those

imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring (paying for) the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical content. The assignment of links, rules, and weights is optional.

UNCLASSIFIED

Security Classification